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GENERAL CHEMISTRY: ATOMS FIRST

Chapter 17 Electrochemistry

Prentice Hall

Oxidation & Reduction (OIL RIG)

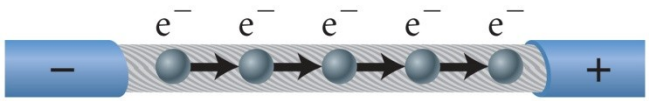
- **oxidation** is the process that occurs when
  - ✓oxidation number of an element increases
  - ✓element loses electrons
  - ✓compound adds oxygen
  - ✓compound loses hydrogen
  - ✓half-reaction has electrons as products
- **reduction** is the process that occurs when
  - ✓oxidation number of an element decreases
  - ✓element gains electrons
  - ✓compound loses oxygen
  - ✓compound gains hydrogen
  - ✓half-reactions have electrons as reactants

Oxidation–Reduction

- oxidation and reduction **occur simultaneously**
- the reactant that reduces another reactant is called the **reducing agent**
- the reactant that oxidizes another reactant is called the **oxidizing agent**

Electrical Current

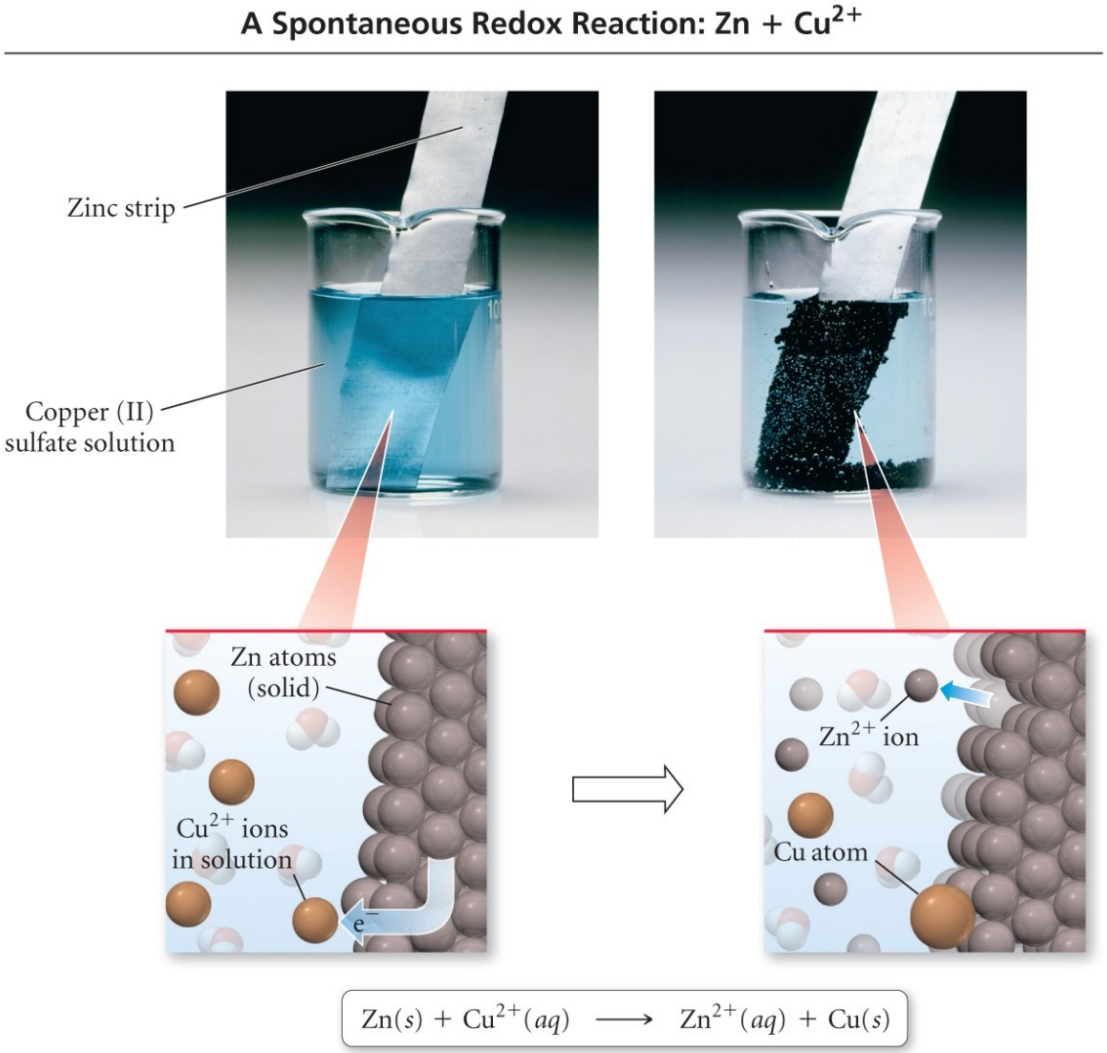
- the current of a liquid stream is measured by the amount of water passing by in a given period of time
- electric current is the amount of electric charge that passes a point in a given period of time
  - ✓ Can be electrons flowing through a wire, or
  - ✓ ions flowing through a solution



Redox Reactions & Current

- redox reactions transfer electrons from one substance to another
- therefore, redox reactions have the potential to generate an electric current
  - ✓ to use that current, we need to separate the oxidation reaction from the reduction reaction

Electric Current Flowing Directly Between $Zn_{(s)}$ and Cu^{2+}



Electrochemical Cells

- **electrochemistry** is the study of redox reactions that produce or require an electric current
- the conversion between chemical energy and electrical energy is carried out in an **electrochemical cell**
- spontaneous redox reactions take place in a **voltaic cell, (aka a galvanic cell)**
- non-spontaneous redox reactions can be made to occur in an **electrolytic cell** by the addition of electrical energy

Galvanic Cells

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

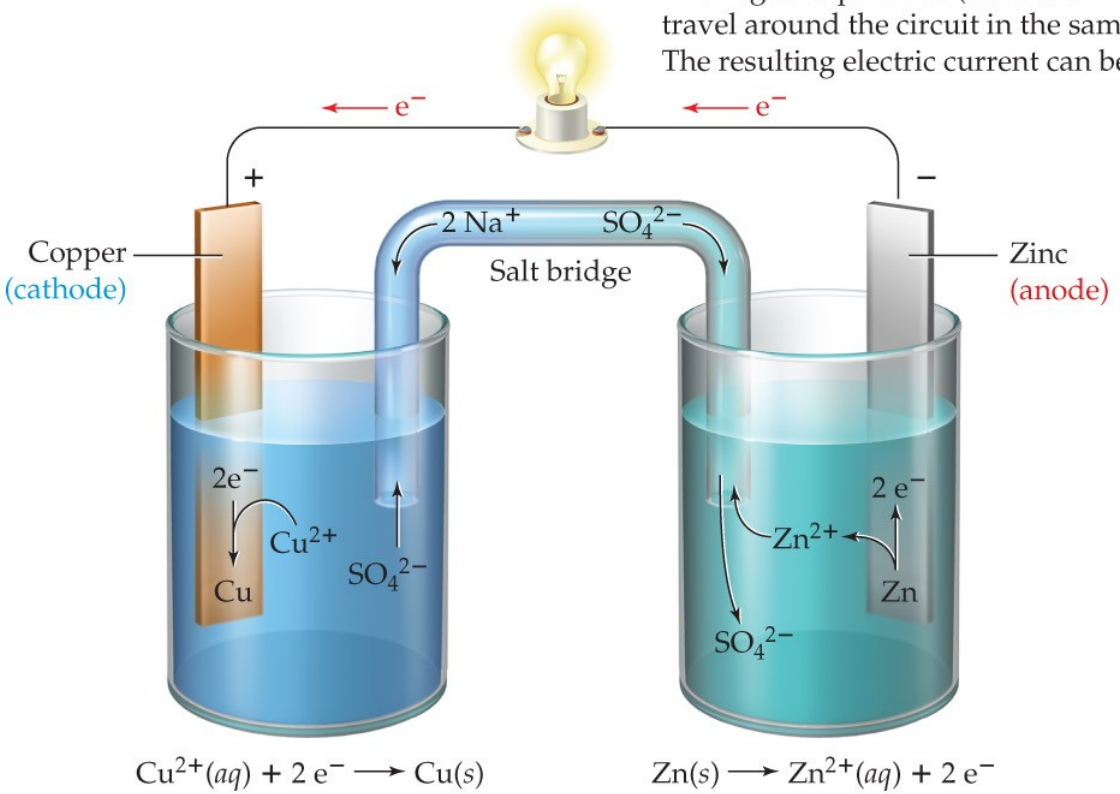
Oxidation half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Galvanic Cells

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The negative particles (electrons in the wire and anions in solution) travel around the circuit in the same counterclockwise direction. The resulting electric current can be used to light a lightbulb.



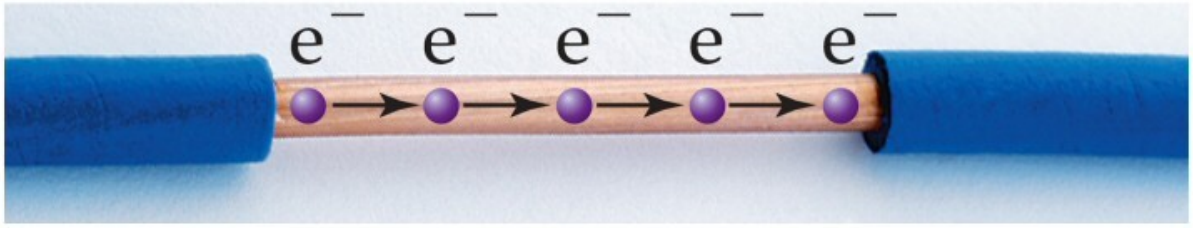
(a)

The salt bridge in part (**a**) is replaced by a porous glass disk that allows ions to flow between the anode and cathode compartments but prevents bulk mixing, which would bring Cu^{2+} ions into direct contact with zinc and short-circuit the cell.

(b)

Electrochemical Cells

- oxidation and reduction reactions kept separate in **half-cells**
- electric circuit made up by:
  - ✓ electron flow through a wire
  - ✓ ion flow through a electrolyte solution or salt bridge between the two halves of the system
- conductive solid (metal or graphite) allows the transfer of electrons - **electrode**



Electrodes

- **Anode**
  - ✓electrode where oxidation occurs
  - ✓anions attracted to it
  - ✓connected to positive end of battery in electrolytic cell
  - ✓loses weight in electrolytic cell
- **Cathode**
  - ✓electrode where reduction occurs
  - ✓cations attracted to it
  - ✓connected to negative end of battery in electrolytic cell
  - ✓gains weight in electrolytic cell
    - ➢electrode where plating takes place in electroplating

Galvanic Cells

- **Anode**:
  - The electrode where oxidation occurs.
  - The electrode where electrons are produced.
  - Is what anions migrate toward.
  - Has a negative sign.
- **Cathode**:
  - The electrode where reduction occurs.
  - The electrode where electrons are consumed.
  - Is what cations migrate toward.
  - Has a positive sign.

Galvanic Cells

Anode half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall cell reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Cell Potential

- the difference in potential energy between the anode and the cathode in a voltaic cell is called the **cell potential**

- the cell potential depends on the relative ease with which the oxidizing agent is reduced at the cathode and the reducing agent is oxidized at the anode

Current

Current = the number of electrons that flow through the system per second

- ✓ Units of current are the Ampere
  - ➢ 1 Ampere = 6.242×10^{18} electrons/second = 1 Coulomb of charge flowing per second
- ✓ Electrode surface area dictates the number of electrons that can flow

Voltage

- the difference in potential energy between the reactants and products is the **potential difference**
  - ✓ units given in volts
    - ➢ 1 volt = 1 J of energy/Coulomb of charge
  - ✓ the voltage needed to drive electrons through the external circuit
- amount of force pushing the electrons through the wire is called the **electromotive force, emf**
- the cell potential under standard conditions is called the **standard emf, $E°_{cell}$**
  - ✓ 25°C, 1 atm for gases, 1 M concentration of solution
  - ✓ sum of the cell potentials for the half-reactions

Cell Notation

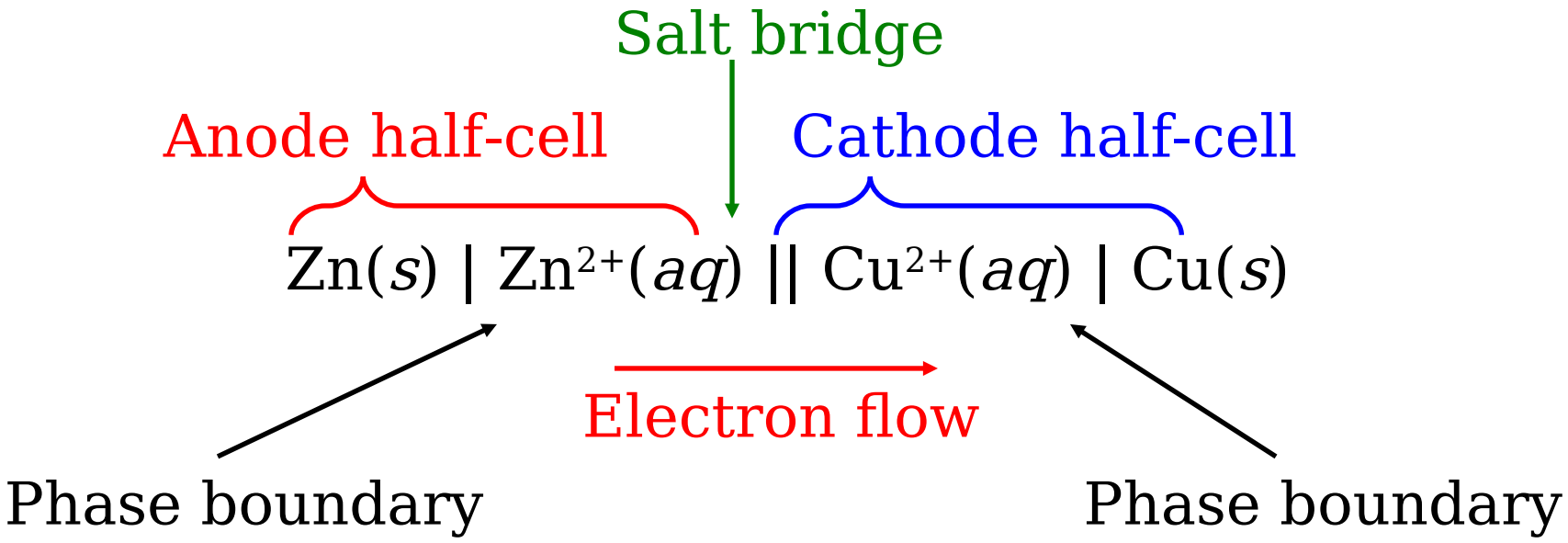
- shorthand description of Voltaic cell
- electrode | electrolyte || electrolyte | electrode
- **oxidation** half-cell on the **left**
- **reduction** half-cell on the **right**
- a single | is a phase barrier
- multiple electrolytes that are in the same phase are separated by a comma
- a double line || denotes a salt bridge

Shorthand Notation for Galvanic Cells

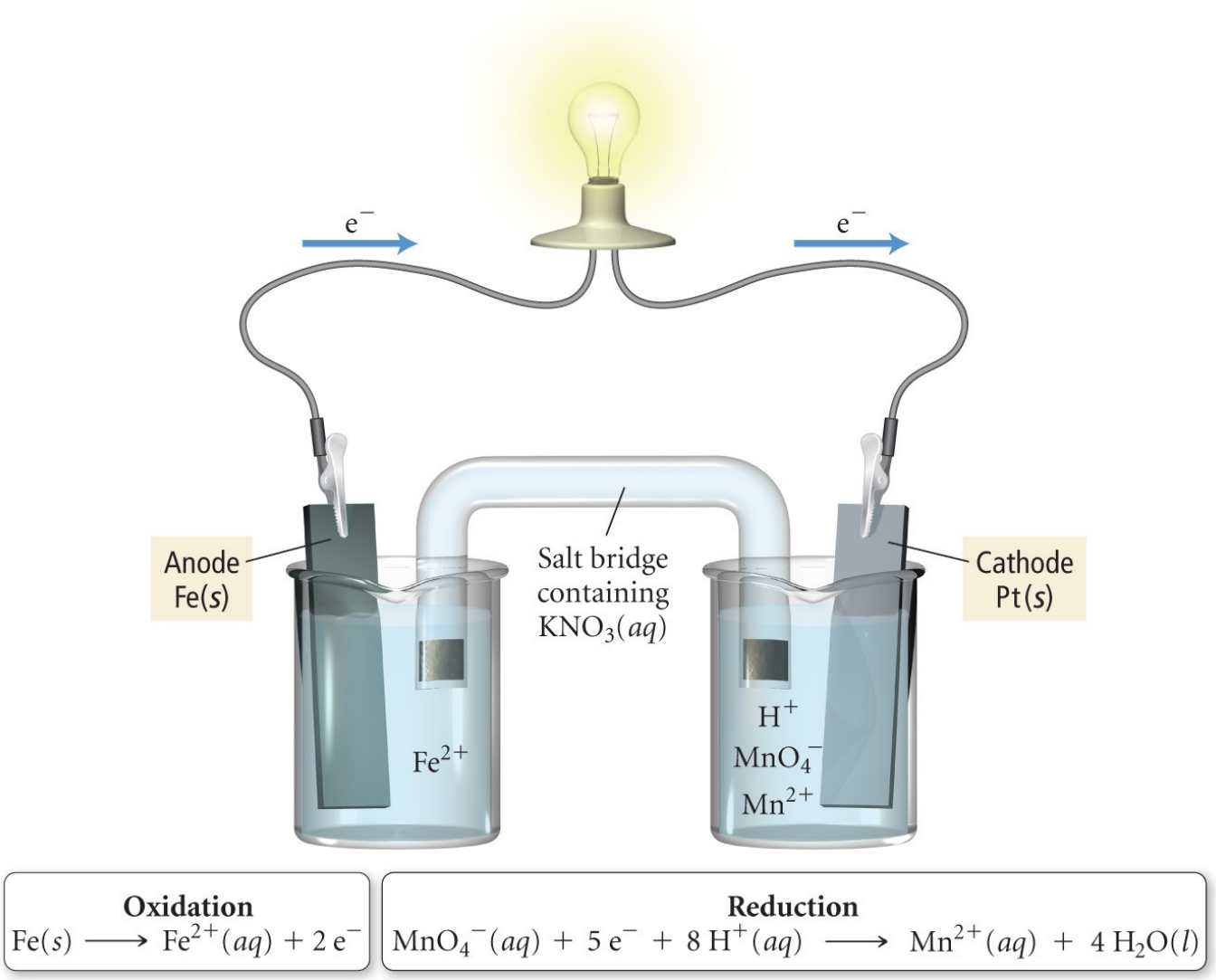
Anode half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall cell reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$



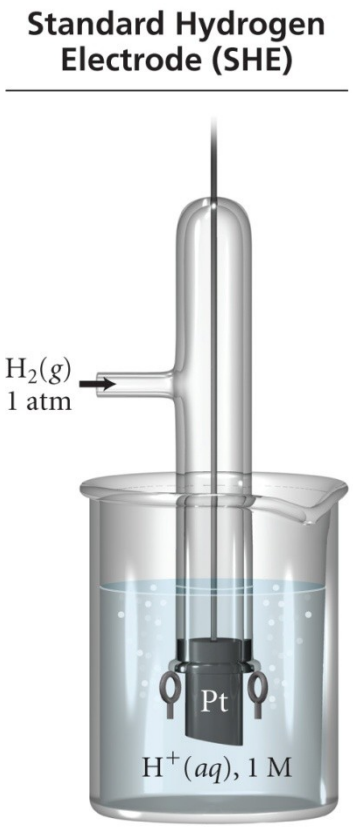
Inert Platinum Electrode



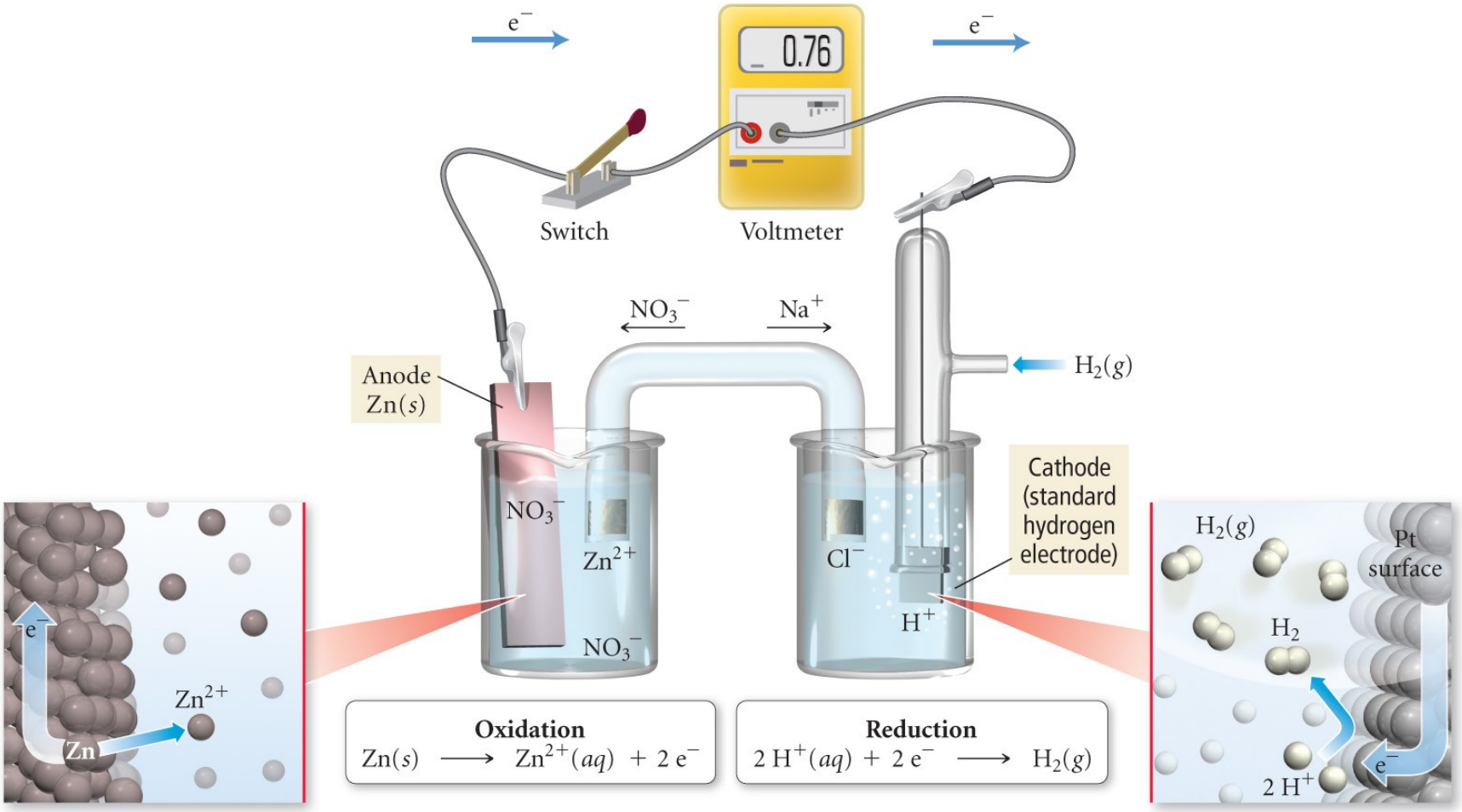
e(s) | $Fe^{2+}(aq)$ || $MnO_4^-(aq)$, $Mn^{2+}(aq)$, $H^+(aq)$ | Pt(*s*)

Standard Reduction Potential

- half-reactions with a strong tendency to occur have large positive half-cell potentials
- when two half-cells are connected, the electrons will flow so that the half-reaction with the stronger tendency will occur
- we cannot measure the absolute tendency of a half-reaction, we can only measure it relative to another half-reaction
- the standard reference point half-reaction is the reduction of H^+ to H_2 under standard conditions
  - ✓ assigned a potential difference = 0 v
  - ✓ **called the standard hydrogen electrode, SHE**



Measuring Half-Cell Potential with the SHE



Half-Cell Potentials

- half-reactions with a stronger tendency toward reduction than the SHE (0 v) have a + value for $E°_{red}$
- half-reactions with a stronger tendency toward oxidation than the SHE have a - value for $E°_{red}$
- $E°_{cell} = E°_{oxidation} + E°_{reduction}$
  - ✓ when adding E° values for the half-cells, **do not multiply** the half-cell E° values, even if you need to multiply the half-reactions' electrons to balance the equation
  - ✓ all standard potentials are given as reduction, so if the half reaction is the oxidation you need to use the opposite sign
    - ➢ $E°_{reduction} \rightarrow -E°_{oxidation}$

TABLE 18.1 Standard Reduction Potentials at 25 °C

Stronger oxidizing agent ↑

Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F^-(aq)$	2.87
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78
$PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2\,e^-$	$\longrightarrow PbSO_4(s) + 2\,H_2O(l)$	1.69
$MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow MnO_2(s) + 2\,H_2O(l)$	1.68
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51
$Au^{3+}(aq) + 3\,e^-$	$\longrightarrow Au(s)$	1.50
$PbO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Pb^{2+}(aq) + 2\,H_2O(l)$	1.46
$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33
$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23
$MnO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	1.21
$IO_3^-(aq) + 6\,H^+(aq) + 5\,e^-$	$\longrightarrow \frac{1}{2}\,I_2(aq) + 3\,H_2O(l)$	1.20
$VO_2^+(aq) + 2\,H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00
$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09
$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow NO(s) + 2\,H_2O(l)$	0.96
$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56
$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52
$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40

Weaker reducing agent ↓

$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$		0.34
$SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow H_2SO_3(aq) + H_2O(l)$		0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$		0.16
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$		0.15
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(s)$		0
$Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s)$		−0.036
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$		−0.13
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$		−0.14
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$		−0.23
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$		−0.40
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$		−0.45
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$		−0.50
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$		−0.76
$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s)$		−0.73
$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$		−0.83
$Mn^{2+}(aq) + 2\,e^- \longrightarrow Mn(s)$		−1.18
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$		−1.66
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$		−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$		−2.71
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$		−2.76
$Ba^{2+}(aq) + 2\,e^- \longrightarrow Ba(s)$		−2.90
$K^+(aq) + e^- \longrightarrow K(s)$		−2.92
$Li^+(aq) + e^- \longrightarrow Li(s)$		−3.04

Weaker oxidizing agent

Stronger reducing agent

Calculate E°_{cell} for the reaction at 25°C

$$Al_{(s)} + NO_3^-{}_{(aq)} + 4\ H^+{}_{(aq)} \rightarrow Al^{3+}{}_{(aq)} + NO_{(g)} + 2\ H_2O_{(l)}$$

Separate the reaction into the oxidation and reduction half-reactions	ox: $Al(s) \rightarrow Al3+(aq) + 3\ e-$ red: $NO3-(aq) + 4\ H+(aq) + 3e- \rightarrow NO(g) +$ $2\ H2O(l)$ **The oxidation half-rxn has a reduction potential of -1.66 v** $E^\circ ox = -E^\circ red = +1.66$ v
find the E° for each half-reaction	**The reduction half-rxn has a reduction potential of +0.96v** $E^\circ red = +0.96$ v **Now add the two half-rxns together** $E^\circ cell = (+1.66\text{ v}) + (+0.96\text{ v}) = +2.62$ v

Predicting Redox Sponteneity and Direction

- Half-rxns at the top of the list have a strong tendency to occur in the forward direction
- Half-rxns at the bottom of the list have a strong tendency to occur in the reverse direction
- Any reduction half-rxn will be spontaneous when paired with the reverse of a half-rxn below it on the table

Predict if the following reaction is spontaneous under standard conditions

$$Fe_{(s)} + Mg^{2+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Mg_{(s)}$$

Separate the reaction into the oxidation and reduction half-reactions	ox: $Fe(s) \rightarrow Fe2+(aq) + 2\ e-$ *Oxidation potential = +0.45* red: $Mg2+(aq) + 2\ e- \rightarrow Mg(s)$ *Reduction potential = −2.37* red: $Mg2+(aq) + 2\ e- \rightarrow Mg(s)$ red: $Fe2+(aq) + 2\ e- \rightarrow Fe(s)$
look up the relative positions of the	since Mg2+ reduction is below Fe2+ reduction, the reaction is **NOT spontaneous** as written

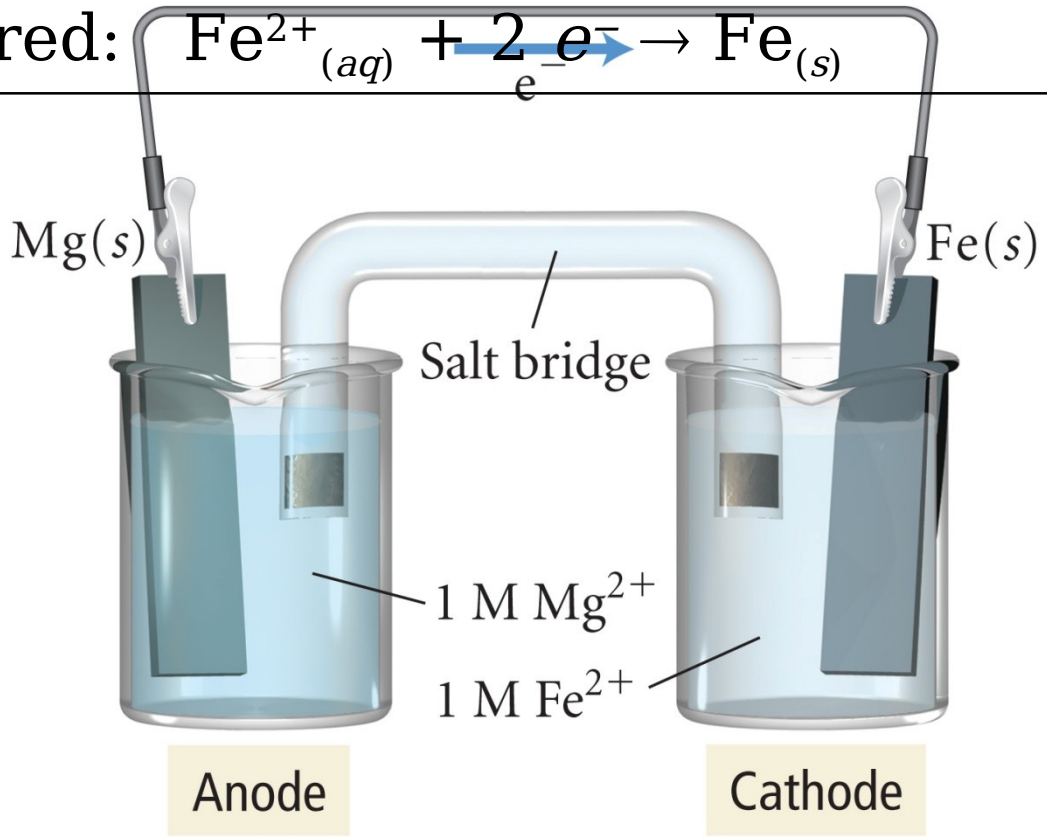
the reaction is spontaneous in the reverse direction

$Mg_{(s)} + Fe^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Fe_{(s)}$

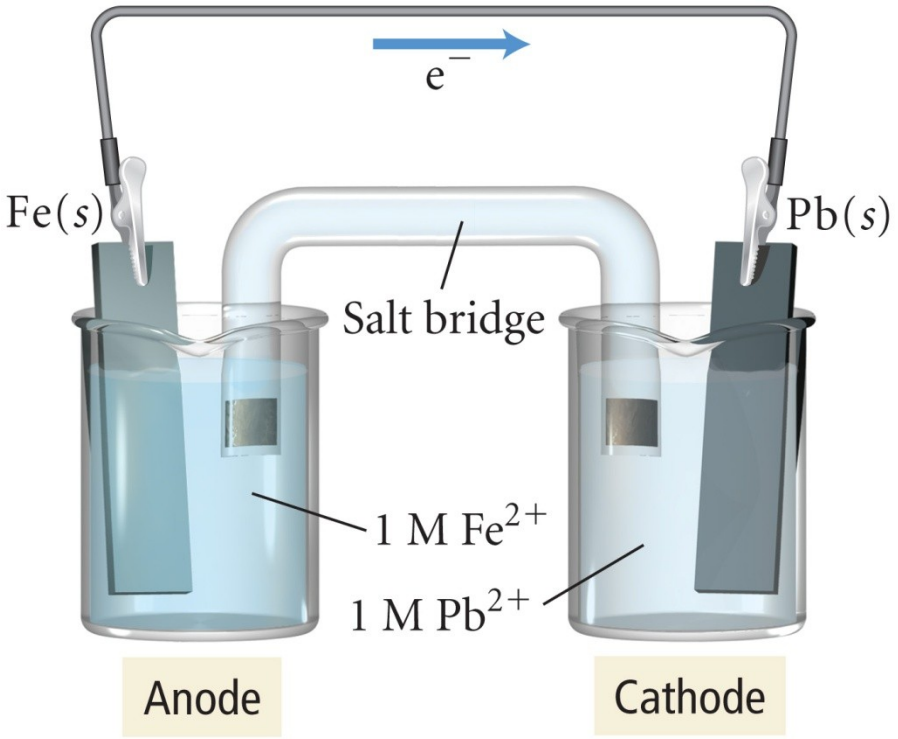
ox: $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2\ e^-$

red: $Fe^{2+}_{(aq)} + 2\ e^- \rightarrow Fe_{(s)}$

sketch the cell and label the parts – oxidation occurs at the anode; electrons flow from anode to cathode



Sketching a Voltaic Cell: $Fe(s) \mid Fe^{2+}(aq) \parallel Pb^{2+}(aq) \mid Pb(s)$ Writing Half-Reactions , Overall Reaction, Determining Cell Potential under Std Conditions.



ox: $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$

$E^\circ = +0.45$ V

red: $Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)$

$E^\circ = -0.13$ V

ot: $Pb^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Pb(s)$

$^\circ = +0.32$ V

More examples

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E^\circ_{red} = -0.23$ v

$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ $E^\circ_{red} = -1.18$ v

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E^\circ_{red} = -0.23$v

$Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$ $E^\circ_{ox} = +1.18$v

+0.95v

$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ $E^\circ_{ox} = +0.23$v

$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ $E^\circ_{red} = -1.18$v

−0.95v

More examples

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E^\circ_{red} = -0.23$ v

$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $E^\circ_{red} = -0.13$ v

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E^\circ_{red} = -0.23$v

$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$ $E^\circ_{ox} = +0.13$v

-0.10v

$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ $E^\circ_{ox} = +0.23$v

$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $E^\circ_{red} = -0.13$v

$+0.10$v

Predicting Whether a Metal Will Dissolve in an Acid

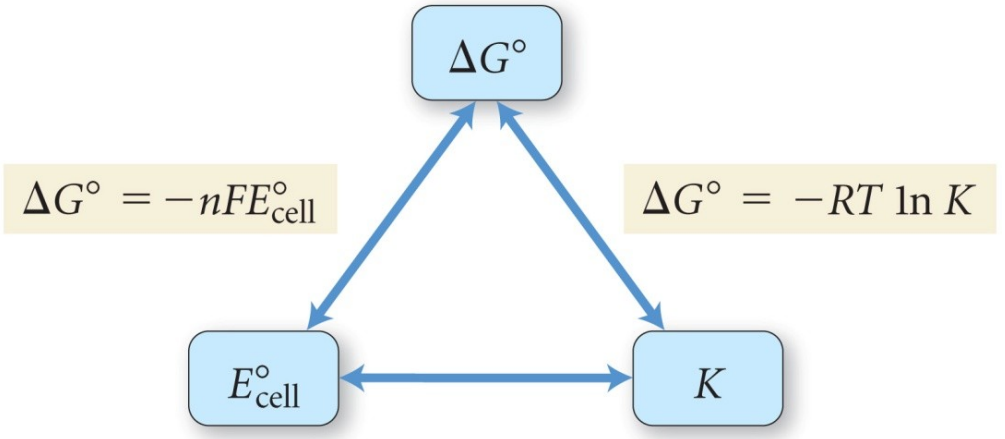
- acids dissolve metals if the reduction of the metal ion is easier than the reduction of $2H^+_{(aq)} \rightarrow H_2 \quad E^o=0v$
- metals whose reduction reaction lies below H^+ reduction on the table will dissolve in acid (since they are negative, the reverse rxn will be positive potential

$Zn(s) + 2\,H^+(aq) \longrightarrow$

$Zn^{2+}(aq) + H_2(g)$

$E°_{cell,}$ $\Delta G°$ and K

- for a spontaneous reaction that proceeds forwards with chemicals in their standard states
  - ✓$\Delta G° < 0$ (negative)
  - ✓$E° > 0$ (positive)
  - ✓$K > 1$ (means ln K = +)



- $\Delta G° = -RT\ln K = -nFE°_{cell}$

$$E°_{cell} = \frac{0.0592\ \text{V}}{n} \log K$$

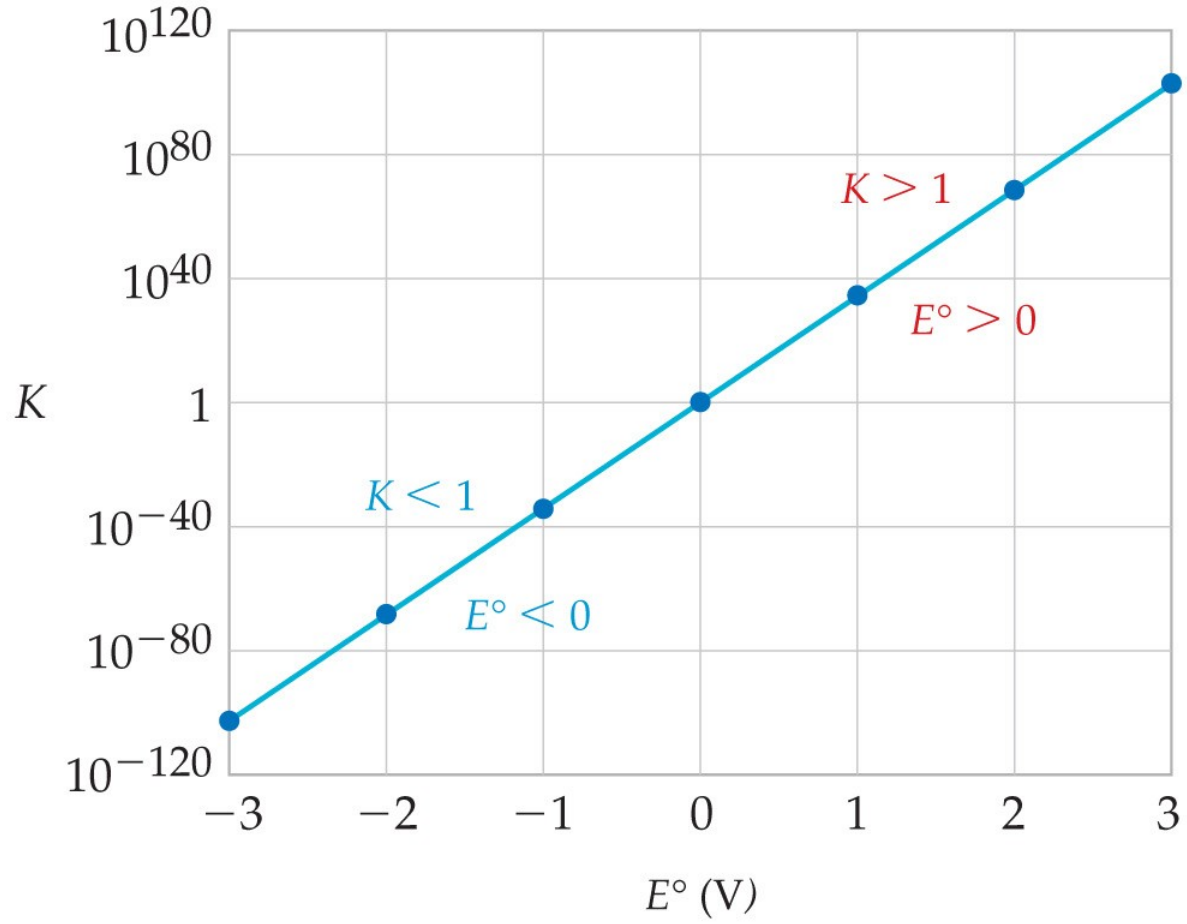
  - ✓n is the number of electrons
  - ✓F = Faraday's Constant = 96,485 C/mol e^-

Electrolytic Cells

TABLE 17.2 Relationship between Cell Potentials E and Free-Energy Changes ΔG

Reaction Type	E	ΔG	Cell Type
Spontaneous	+	−	Galvanic
Nonspontaneous	−	+	Electrolytic
Equilibrium	0	0	Dead battery

Standard Cell Potentials and Equilibrium Constants



Standard Cell Potentials and Equilibrium Constants

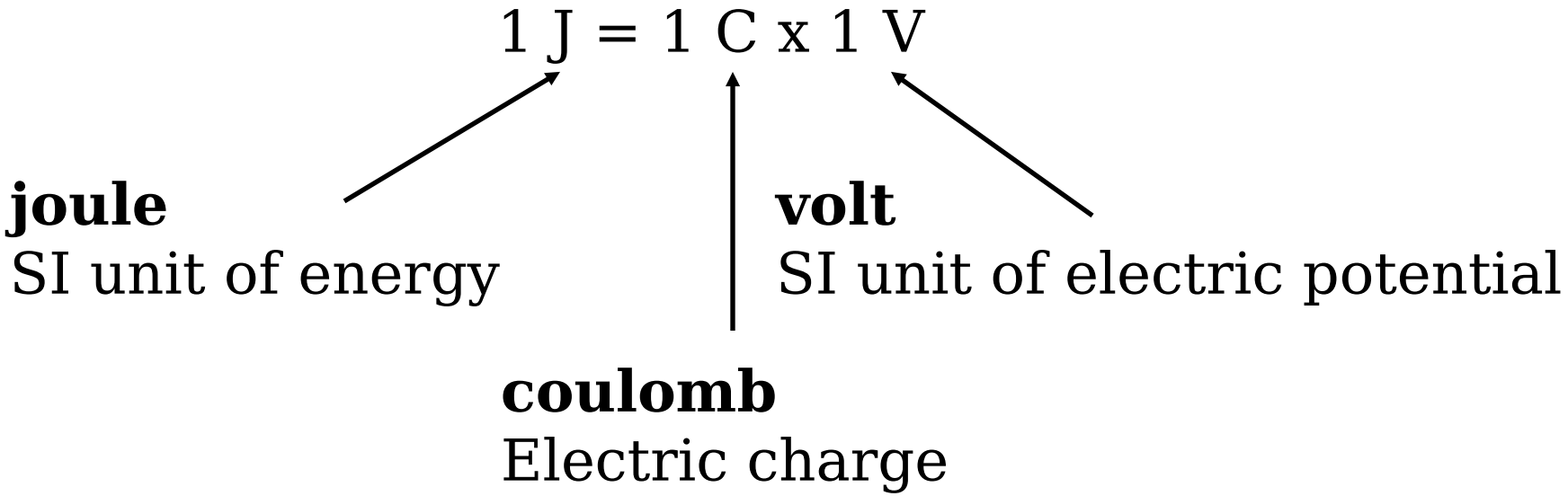
Three methods to determine equilibrium constants:

1. K from concentration data: $K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$

2. K from thermochemical data: $\ln K = \frac{-\Delta G^\circ}{RT}$

3. K from electrochemical data: $\ln K = \frac{nFE^\circ}{RT}$

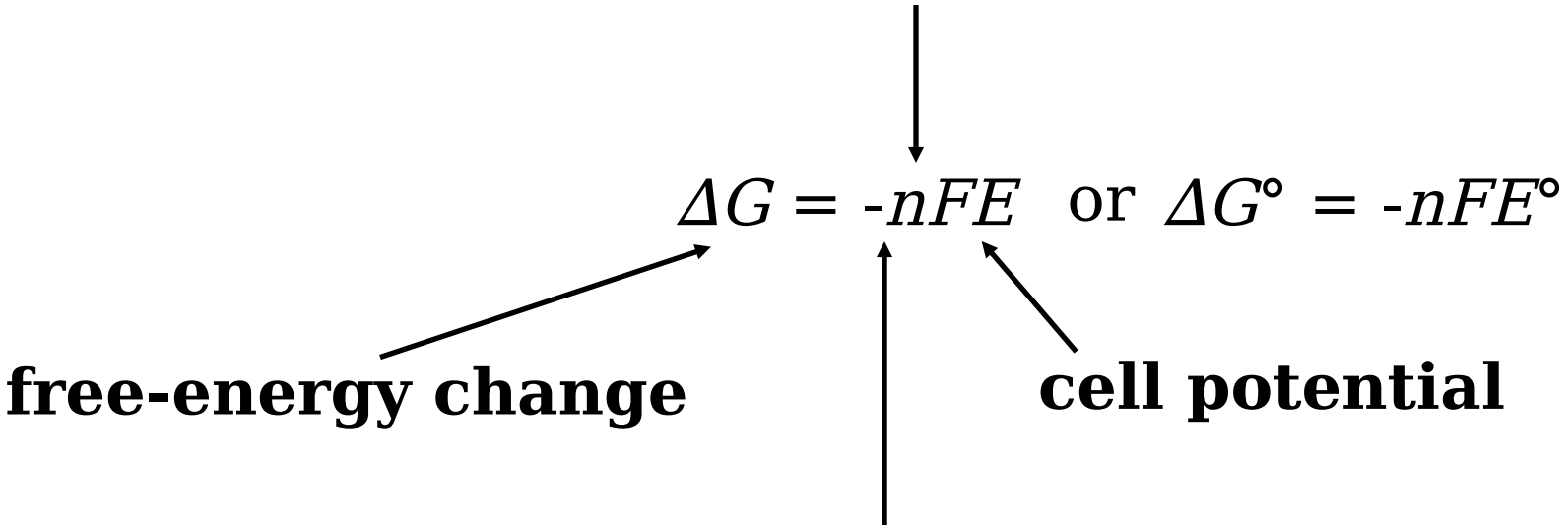
Cell Potentials and Free-Energy Changes for Cell Reactions



1 coulomb is the amount of charge transferred when a current of 1 ampere flows for 1 second.

Cell Potentials and Free-Energy Changes for Cell Reactions

faraday or **Faraday constant**
the electric charge on 1 mol of electrons
96,500 C/mol e^-



Cell Potentials and Free-Energy Changes for Cell Reactions

The standard cell potential at 25 °C is 1.10 V for the reaction:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Calculate the standard free-energy change for this reaction at 25 °C.

$$\Delta G° = -nFE°$$

$$= -(2 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{\text{mol } e^-}\right)(1.10 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C V}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$\Delta G° = \boxed{-212 \text{ kJ}}$$

Calculate ΔG° for the reaction

$$I_{2(s)} + 2\ Br^-_{(aq)} \rightarrow Br_{2(l)} + 2\ I^-_{(aq)}$$

Concept Plan: $E°_{ox}, E°_{red}$ → $E°_{cell}$ → ΔG

Given:	$I_{2(s)} + 2\ Br^-_{(aq)} \rightarrow Br_{2(l)} + 2\ I^-_{(aq)}$
Find:	$\Delta G°$, (J)
Relationships:	$E°_{cell} = E°_{ox} + E°_{red}$ $\quad \Delta G° = -nFE°_{cell}$
Solve:	ox: $2\ Br^-_{(aq)} \rightarrow Br_{2(l)} + 2\ e^-$ $\quad E° = -1.09$ v red: $I_{2(l)} + 2\ e^- \rightarrow 2\ I^-_{(aq)}$ $\quad E° = +0.54$ v tot: $I_{2(l)} + 2Br^-_{(aq)} \rightarrow 2I^-_{(aq)} + Br_{2(l)}$ $\quad E° = -0.55$ v $\Delta G° = -\left(2\ \text{mole}\ e^-\right)\left(96{,}485\ \frac{C}{\text{mole}\ e^-}\right)\left(-0.55\ \frac{J}{C}\right)$ $\Delta G° = +1.1 \times 10^5\ J$
Answer:	since ΔG° is +, the reaction is not spontaneous in the forward direction under standard conditions

Calculate K at 25°C for the reaction

$$Cu_{(s)} + 2\ H^+_{(aq)} \rightarrow H_{2(g)} + Cu^{2+}_{(aq)}$$

Concept Plan: $E°_{ox}$, $E°_{red}$ → $E°_{cell}$ → K

Given:	$Cu_{(s)} + 2\ H^+_{(aq)} \rightarrow H_{2(g)} + Cu^{2+}_{(aq)}$
Find:	K
Relationships:	$E°_{cell} = E°_{ox} + E°_{red}$ $\qquad E°_{cell} = \frac{0.0592\,V}{n} \log K$
Solve:	ox: $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2\ e^-$ $\qquad E° = -0.34$ v red: $2\ H^+_{(aq)} + 2\ e^- \rightarrow H_{2(aq)}$ $\qquad E° = +0.00$ v tot: $Cu_{(s)} + 2H^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + H_{2(g)}$ $E° = -0.34$
	$E°_{cell} \frac{n}{0.0592\,V} = \log K$ $\qquad \log K = (-0.34\,V) \frac{(2\,mole\,e^-)}{0.0592\,V} = -11.5$
	$K = 10^{-11.5} = 3.2 \times 10^{-12}$
Answer:	since K < 1, the position of equilibrium lies far to the left under standard conditions

The Nernst Equation - Nonstandard Conditions (other than 1M concentration)

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Using: $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$

Nernst Equation: $E = E^\circ - \dfrac{RT}{nF} \ln Q$ **or** $E = E^\circ - \dfrac{\mathbf{2.303}RT}{nF} \log Q$

since 2.303RT/F = 0.0592

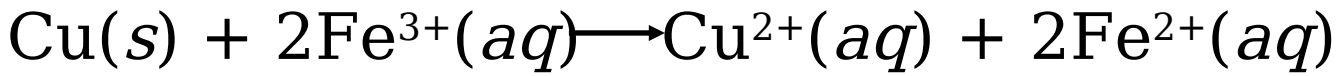
The equation becomes

$$E = E^\circ - \frac{\mathbf{0.0592\ V}}{n} \log Q$$ in volts, at 25°C

Note: when Q = K, E = 0

The Nernst Equation

Consider a galvanic cell that uses the reaction:



What is the potential of a cell at 25 °C that has the following ion concentrations?

$[Fe^{3+}] = 1.0 \times 10^{-4}$ M $[Cu^{2+}] = 0.25$ M $[Fe^{2+}] = 0.20$ M

The Nernst Equation

$$E = E° - \frac{0.0592\ \text{V}}{n} \log Q$$

Calculate $E°$:

$$\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{e}^- \qquad E° = -0.34\ \text{V}$$

$$\text{Fe}^{3+}(aq) + \text{e}^- \longrightarrow \text{Fe}^{2+}(aq) \qquad E° = 0.77\ \text{V}$$

$$E°_{\text{cell}} = -0.34\ \text{V} + 0.77\ \text{V} = 0.43\ \text{V}$$

The Nernst Equation

$$E = E° - \frac{0.0592\ \text{V}}{n} \log Q$$

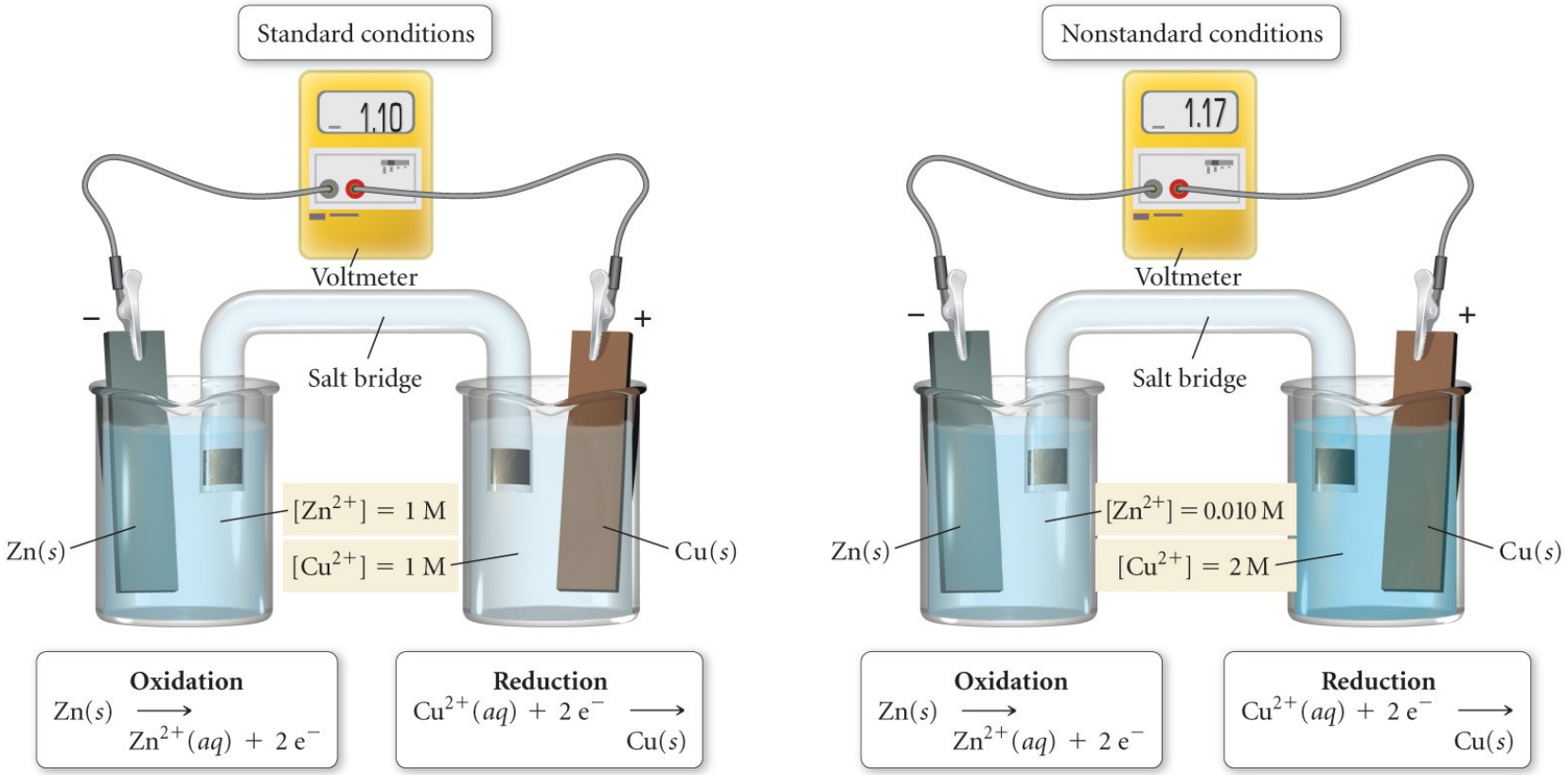
Calculate *E*:

$$E = E° - \left(\frac{0.0592\ \text{V}}{n}\right) \log \frac{[\text{Cu}^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

$$= 0.43\ \text{V} - \left(\frac{0.0592\ \text{V}}{2}\right) \log \left(\frac{(0.25)(0.20)^2}{(1.0 \times 10^{-4})^2}\right)$$

$$E = \boxed{0.25\ \text{V}}$$

E° at Nonstandard Conditions



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Calculate E_{cell} at 25°C for the reaction

$3\,Cu_{(s)} + 2\,MnO_4^-{}_{(aq)} + 8\,H^+{}_{(aq)} \rightarrow 2\,MnO_{2(s)} + 3Cu^{2+}{}_{(aq)} + 4\,H_2O_{(l)}$

Concept Plan: $E°_{ox}, E°_{red}$ → $E°_{cell}$ → E_{cell}

Given:	$3\,Cu_{(s)} + 2\,MnO_4^-{}_{(aq)} + 8\,H^+{}_{(aq)} \rightarrow 2\,MnO_{2(s)} + 3Cu^{2+}{}_{(aq)} + 4\,H_2O_{(l)}$
Find:	$[Cu^{2+}] = 0.010$ M, $[MnO_4^-] = 2.0$ M, $[H^+] = 1.0$ M
Relationships:	E_{cell} $\quad E°_{cell} = E°_{ox} + E°_{red}$ $\quad E_{cell} = E°_{cell} - \frac{0.0592\,V}{n}\log Q$
Solve:	ox: $Cu_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + 2\,e^-\}$x3 $\quad E° = -0.34$ v
	: $MnO_4^-{}_{(aq)} + 4\,H^+{}_{(aq)} + 3\,e^- \rightarrow MnO_{2(s)} + 2\,H_2O_{(l)}\}$x2 $\quad E° = +1.6$
	$3\,Cu_{(s)} + 2\,MnO_4^-{}_{(aq)} + 8\,H^+{}_{(aq)} \rightarrow 2\,MnO_{2(s)} + 3Cu^{2+}{}_{(aq)} + 4\,H_2O_{(l)})$ $E° = +$
	$E_{cell} = E°_{cell} - \frac{0.0592\,V}{n}\log Q$ $\quad E_{cell} = E°_{cell} - \frac{0.0592\,V}{n}\log\frac{[Cu^{2+}]^3}{[MnO_4^-]^3[H^+]^8}$
	$E_{cell} = 1.34\text{V} - \frac{0.0592\,V}{6}\log\frac{[0.010]^3}{[2.0]^3[1.0]^8} = 1.41\text{V}$
Check:	units are correct, $E_{cell} > E°_{cell}$ as expected because $[MnO_4^-] > 1$ M and $[Cu^{2+}] < 1$ M

Concentration Cells

- a spontaneous reaction can occur when the redox reaction is based on the same half-reaction proceeding in opposite directions.
  - ✓ This requires the electrolyte concentrations to be different in the half cells

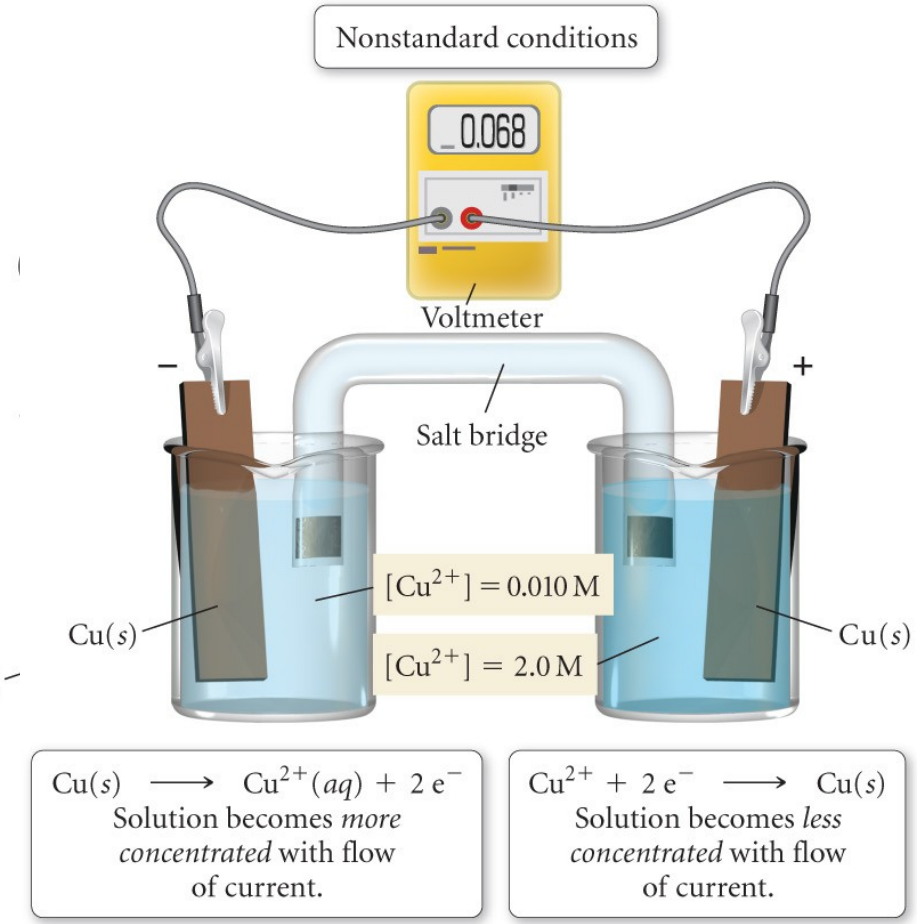
- the difference in energy potential is due to the fact that the more concentrated solution has lower entropy than the less concentrated

- electrons will flow from the electrode in the less concentrated solution to the electrode in the more concentrated solution

Concentration Cell

when the cell concentrations are equal
there is no difference in energy between the half-cells and no electrons flow

when the cell concentrations are different, electrons flow from the side with the less concentrated solution (anode) to the side with the more concentrated solution (cathode)



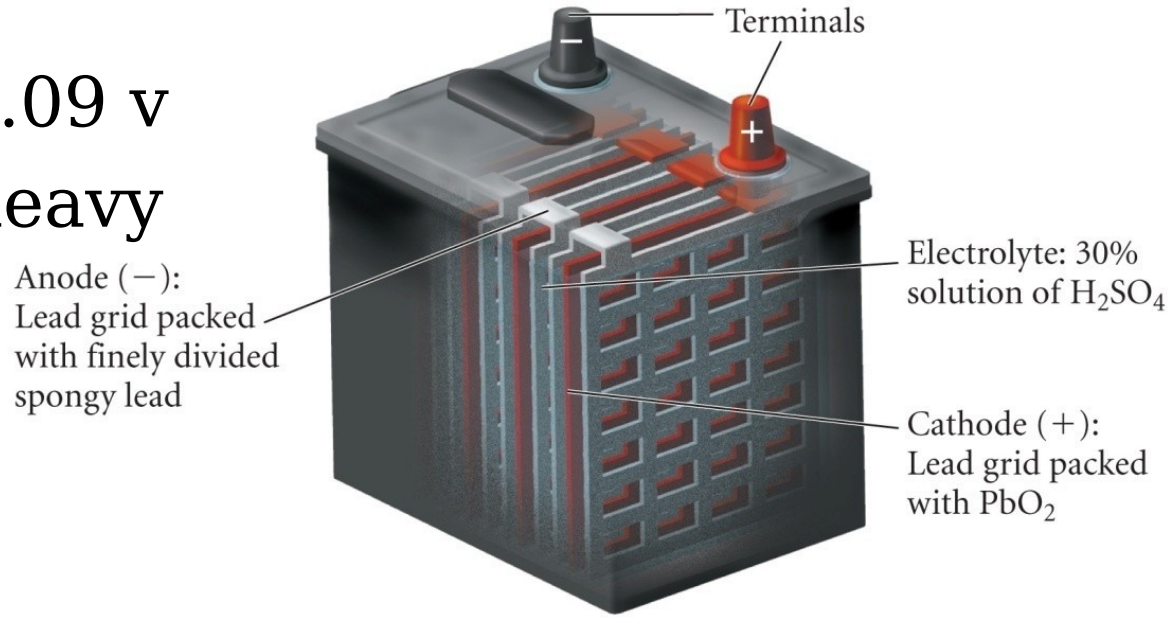
Anode

Cathode

$Cu(s) \mid Cu^{2+}_{(aq)}\ (0.010\ M) \parallel Cu^{2+}_{(aq)}\ (2.0\ M) \mid Cu(s)$

Lead Storage Battery

- 6 cells in series
- electrolyte = 30% H_2SO_4
- cell voltage = 2.09 v
- rechargeable, heavy



Batteries

Lead Storage Battery

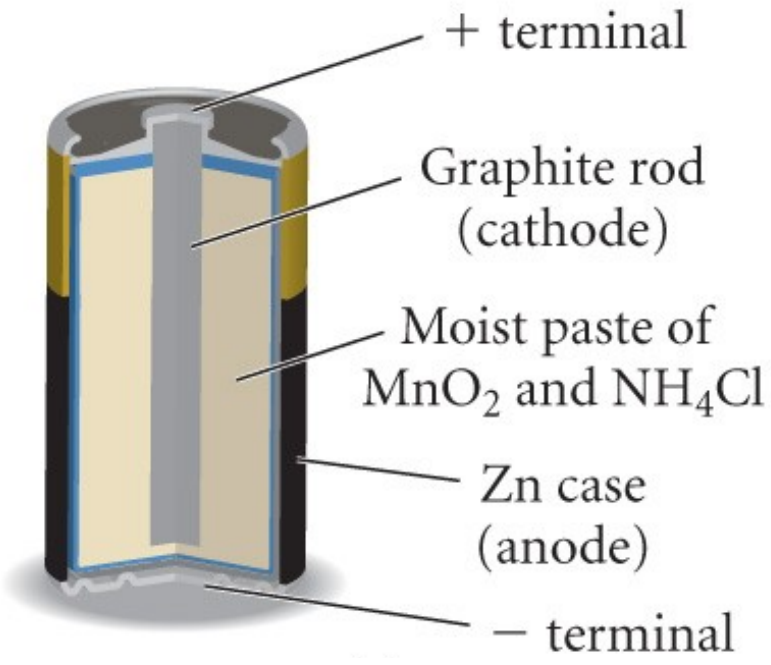
Anode: $Pb(s) + HSO_4^{1-}(aq) \rightarrow PbSO_4(s) + H^{1+}(aq) + 2e^-$

Cathode: $PbO_2(s) + 3H^{1+}(aq) + HSO_4^{1-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall: $Pb(s) + PbO_2(s) + 2H^{1+}(aq) + 2HSO_4^{1-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

LeClanche' Acidic Dry Cell

- electrolyte in paste form
  - ✓ $ZnCl_2 + NH_4Cl$
- cell voltage = 1.5 v
- expensive, non-rechargeable, heavy, easily corroded



Batteries

Dry-Cell Batteries

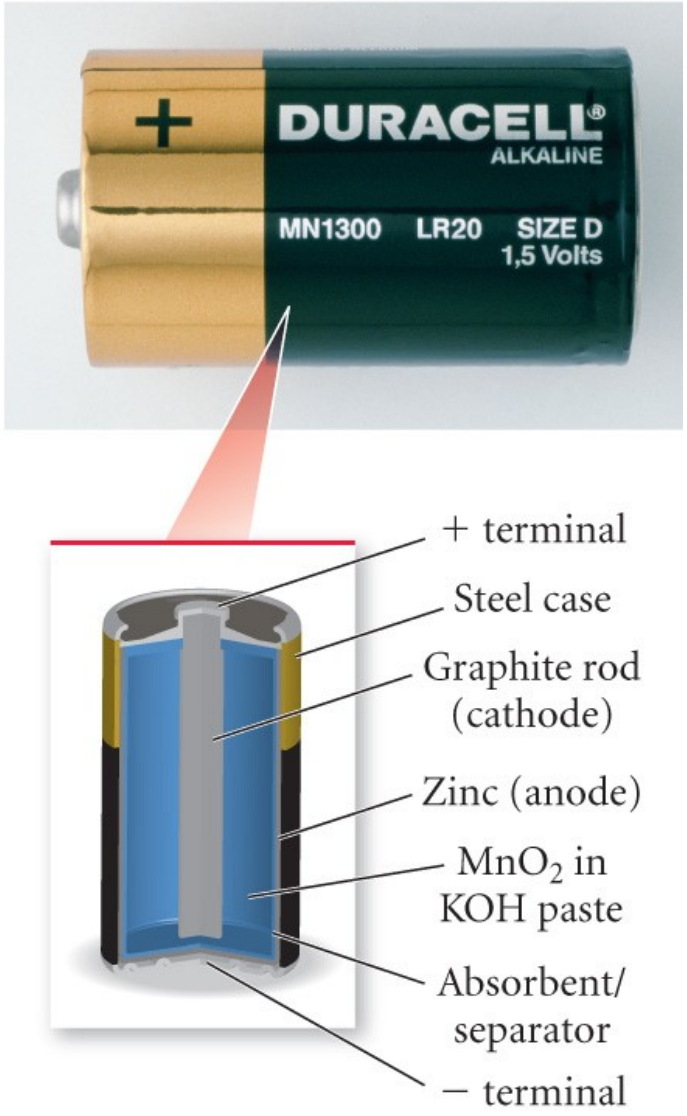
Leclanché cell

Anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode: $2MnO_2(s) + 2NH_4^{1+}(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Alkaline Dry Cell

- same basic cell as acidic dry cell, except electrolyte is alkaline KOH paste
- cell voltage = 1.54 v
- longer shelf life than acidic dry cells and rechargeable, little corrosion of zinc



Batteries

Dry-Cell Batteries

Alkaline cell

Anode: $Zn(s) + 2OH^{1-}(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode: $2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^{1-}(aq)$

NiCad Battery

Nickel-Cadmium Batteries

Anode: $Cd(s) + 2OH^{1-}(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $NiO(OH)(s) + H_2O(l) + e^- \longrightarrow Ni(OH)_2(s) + OH^{1-}(aq)$

- electrolyte is concentrated KOH solution
- cell voltage = 1.30 v
- rechargeable, long life, light – however recharging incorrectly can lead to battery breakdown

Ni-MH Battery

Nickel-Metal Hydride (“*NiMH*”) Batteries

Anode: $MH_{ab}(s) + OH^{1-}(aq) \longrightarrow M(s) + H_2O(l) + e^-$

Cathode: $NiO(OH)(s) + H_2O(l) + e^- \longrightarrow Ni(OH)_2(s) + OH^{1-}(aq)$

Overall: $MH_{ab}(s) + NiO(OH)(s) \longrightarrow M(s) + Ni(OH)_2(s)$

- electrolyte is concentrated KOH solution
- cell voltage = 1.30 v
- rechargeable, long life, light, more environmentally friendly than NiCad, greater energy density than NiCad

Lithium Ion Battery beyond the scope of this chapter

- electrolyte is concentrated KOH solution
- anode = graphite impregnated with Li ions
- cathode = Li - transition metal oxide
  - ✓ reduction of transition metal
- work on Li ion migration from anode to cathode causing a corresponding migration of electrons from anode to cathode
- rechargeable, long life, very light, more environmentally friendly, greater energy density

Batteries

Lithium and Lithium Ion Batteries

Lithium

Anode: $x\mathrm{Li}(s) \longrightarrow x\mathrm{Li}^{1+}(soln) + x\mathrm{e}^-$

Cathode: $\mathrm{MnO_2}(s) + x\mathrm{Li}^{1+}(soln) + x\mathrm{e}^- \longrightarrow \mathrm{Li}_x\mathrm{MnO_2}(s)$

Lithium Ion

Anode: $\mathrm{Li}_x\mathrm{C_6}(s) \longrightarrow x\mathrm{Li}^{1+}(soln) + 6\mathrm{C}(s) + x\mathrm{e}^-$

Cathode: $\mathrm{Li}_{1-x}\mathrm{CoO_2}(s) + x\mathrm{Li}^{1+}(soln) + x\mathrm{e}^- \longrightarrow \mathrm{LiCoO_2}(s)$

TABLE 18.2 Energy Density and Overcharge Tolerance of Several Rechargeable Batteries

Battery Type	Energy Density (W · h/kg)	Overcharge Tolerance
NiCad	45–80	Moderate
NiMH	60–120	Low
Li ion	110–160	Low
Pb storage	30–50	High

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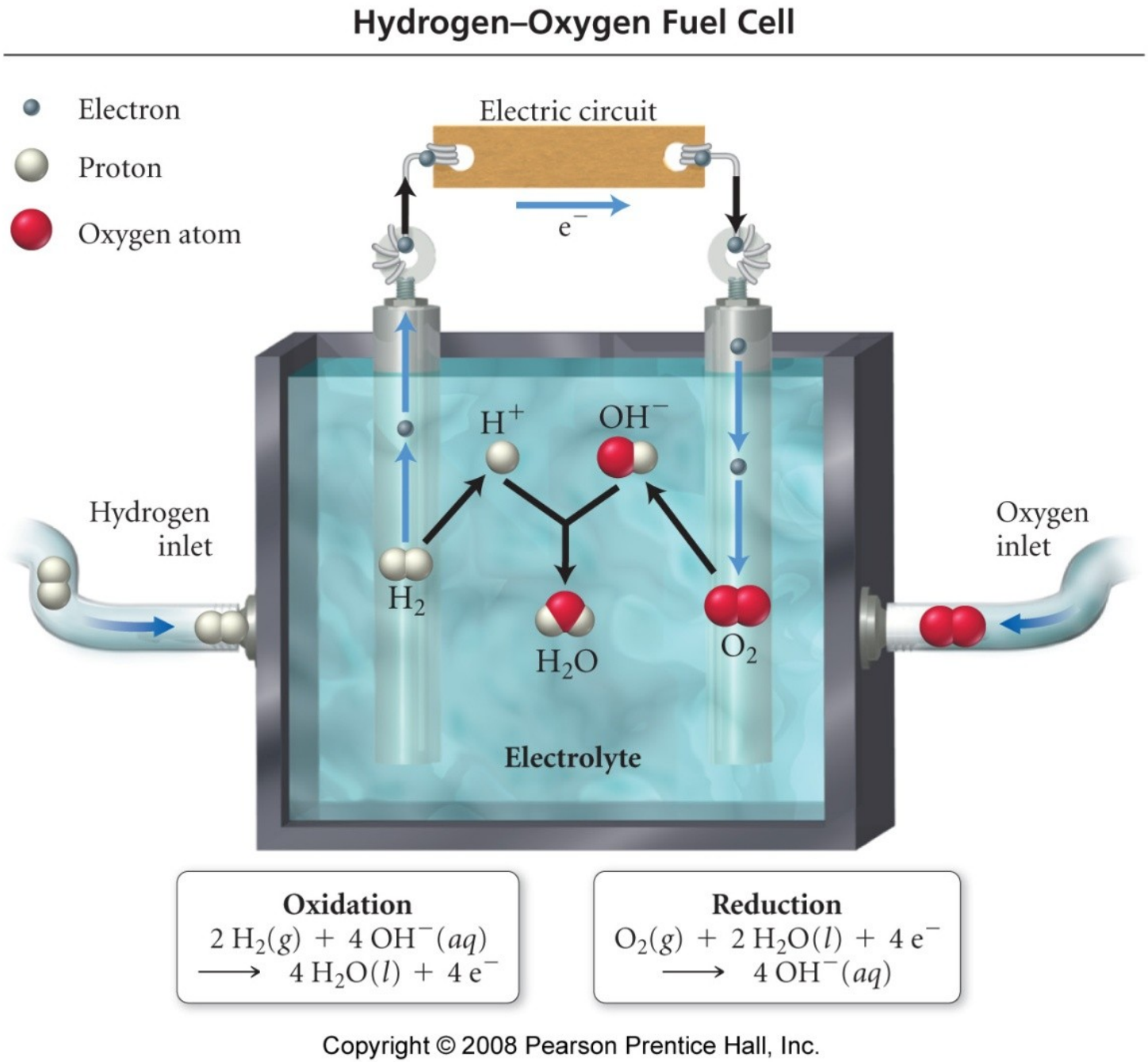
Fuel Cells



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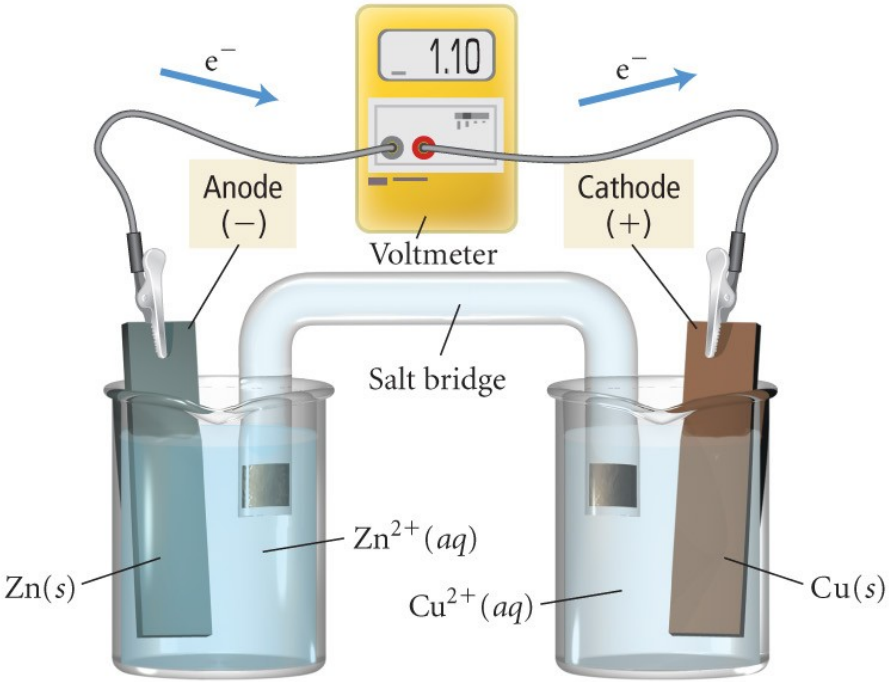
Fuel Cells

- like batteries in which reactants are constantly being added
  - ✓ so it never runs down!
- Anode and Cathode both Pt coated metal
- Electrolyte is OH^- solution
- Anode Reaction: $2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O(l) + 4\ e^-$
- Cathode Reaction: $O_2 + 4\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

Electrolytic Cell

- uses electrical energy to overcome the energy barrier and cause a non-spontaneous reaction to proceed
  - ✓ must be DC source
- the + terminal of the battery = anode
- the - terminal of the battery = cathode
- cations attracted to the cathode, anions to the anode
- cations pick up electrons from the cathode and are reduced, anions release electrons to the anode and are oxidized
- some electrolysis reactions require more voltage than E_{tot}, called the **overvoltage**

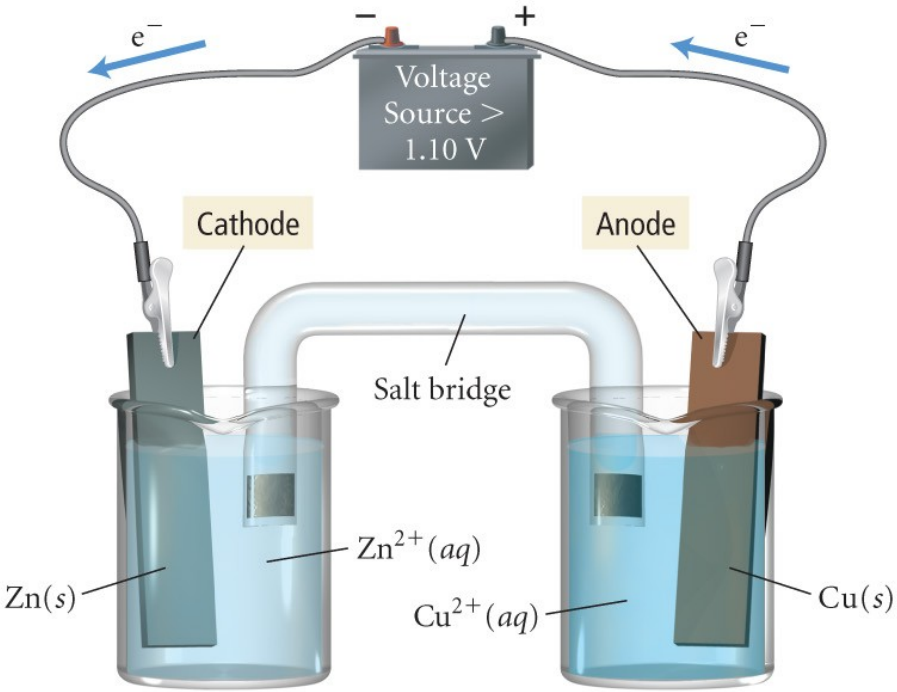
Voltaic Cell



$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$

$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

Electrolytic Cell



$Zn^{2+}(aq) + 2\,e^- \longleftarrow Zn(s)$

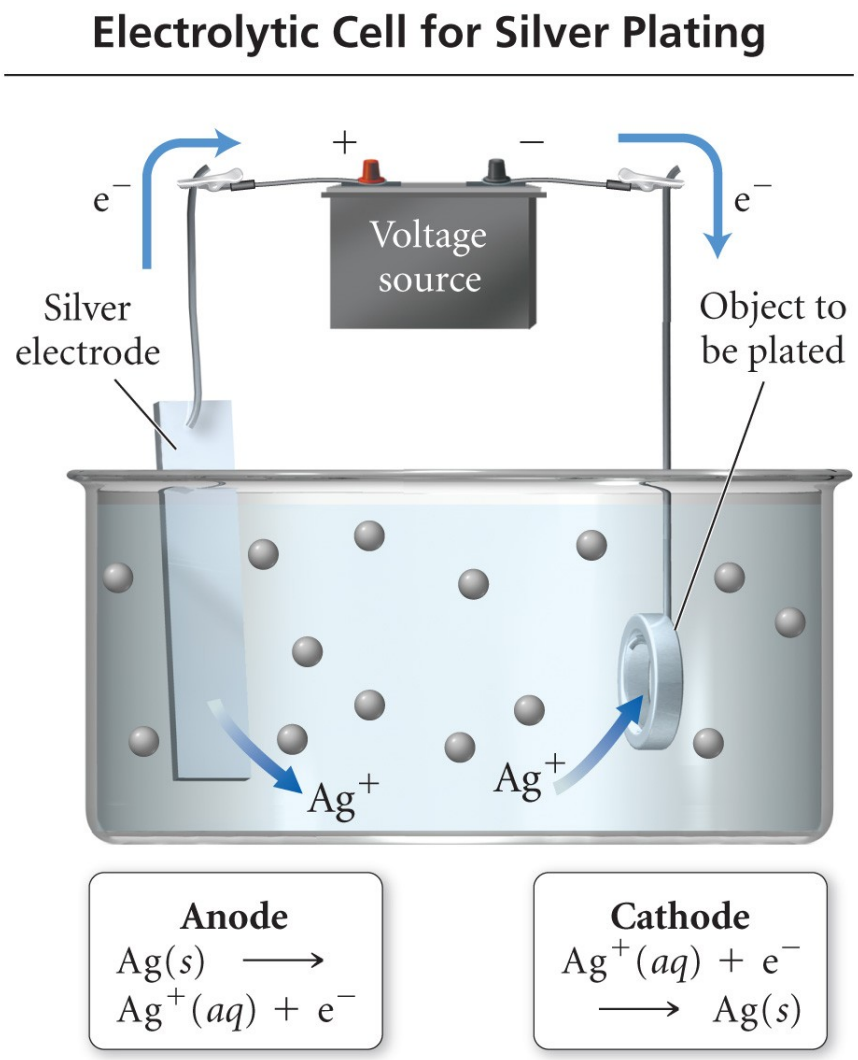
$Cu(s) \longleftarrow Cu^{2+}(aq) + 2\,e^-$

electroplating

In electroplating, the work piece is the cathode.

Cations are reduced at cathode and plate to the surface of the work piece.

The anode is made of the plate metal. The anode oxidizes and replaces the

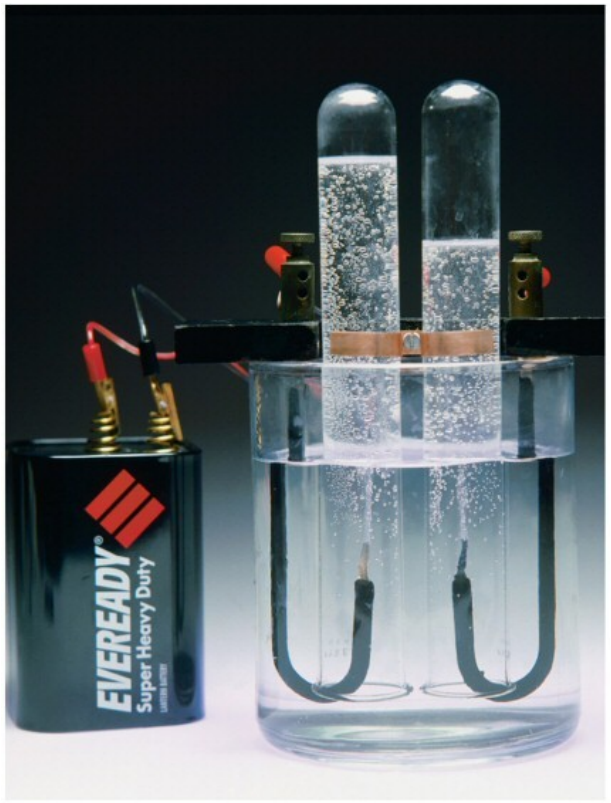


Electrochemical Cells

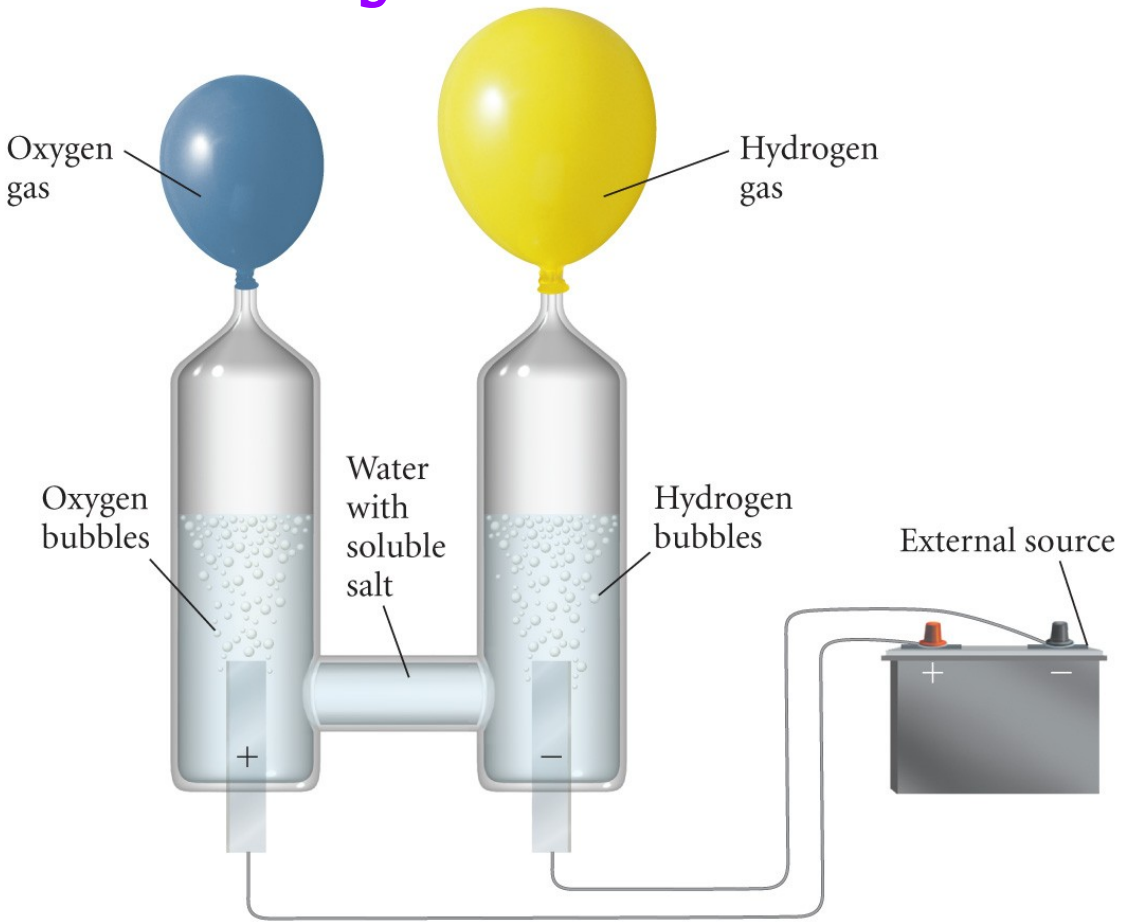
- in all electrochemical cells, oxidation occurs at the anode, reduction occurs at the cathode
- in voltaic cells,
  - ✓ anode is the source of electrons and has a (−) charge
  - ✓ cathode draws electrons and has a (+) charge
- in electrolytic cells
  - ✓ electrons are drawn off the anode, so it must have a place to release the electrons, the + terminal of the battery
  - ✓ electrons are forced toward the cathode, so it must have a source of electrons, the − terminal of the battery

Electrolysis

- electrolysis is the process of using electricity to break a compound apart
- electrolysis is done in an electrolytic cell
- electrolytic cells can be used to separate elements from their compounds
  - ✓ generate H_2 from water for fuel cells
  - ✓ recover metals from their ores



Electrolysis of Water



Anode

$$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+ + 4\,e^-$$

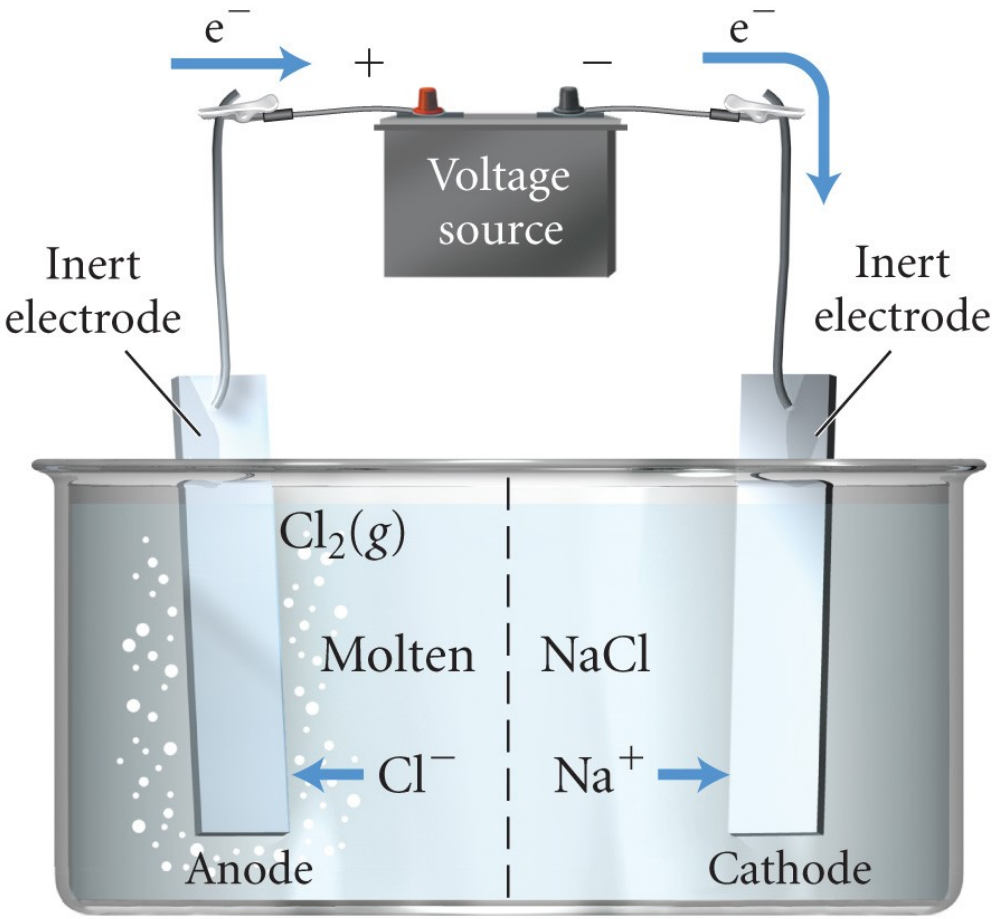
Cathode

$$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$$

Electrolysis of Pure Compounds

- must be in molten (liquid) state
- electrodes normally graphite
- cations are reduced at the cathode to metal element
- anions oxidized at anode to nonmetal element

Electrolysis of $NaCl_{(l)}$



$2\ Cl^-(l) \longrightarrow Cl_2(g) + 2\ e^-$

$2\ Na^+(l) + 2\ e^- \longrightarrow 2\ Na(s)$

Electrolysis

Electrolysis of Molten Sodium Chloride

Anode: $2Cl^{1-}(l) \longrightarrow Cl_2(g) + 2e^-$

Cathode: $2Na^{1+}(l) + 2e^- \longrightarrow 2Na(l)$

Overall: $2Na^{1+}(l) + 2Cl^{1-}(l) \longrightarrow 2Na(l) + Cl_2(g)$

Mixtures of Ions

- when more than one cation is present, the cation that is easiest to reduce will be reduced first at the cathode
  - ✓least negative or most positive $E°_{red}$

- when more than one anion is present, the anion that is easiest to oxidize will be oxidized first at the anode
  - ✓least negative or most positive $E°_{ox}$

Electrolysis of Aqueous Solutions

- Complicated by more than one possible oxidation and reduction
- possible cathode reactions
  - ✓ reduction of cation to metal
  - ✓ reduction of water to H_2
    - ➢ $2\ H_2O + 2\ e^{-1} \rightarrow H_2 + 2\ OH^{-1}$ $E° = -0.83$ v @ stand. cond.
      $E° = -0.41$ v @ pH 7
- possible anode reactions
  - ✓ oxidation of anion to element
  - ✓ oxidation of H_2O to O_2
    - ➢ $2\ H_2O \rightarrow O_2 + 4e^{-1} + 4H^{+1}$ $E° = -1.23$ v @ stand. cond.
      $E° = -0.82$ v @ pH 7
  - ✓ oxidation of electrode
    - ➢ particularly Cu
    - ➢ graphite doesn't oxidize
- half-reactions that lead to least negative E_{tot} will occur
  - ✓ unless overvoltage changes the conditions

Electrolysis of $NaI_{(aq)}$ with Inert Electrodes***

ossible oxidations

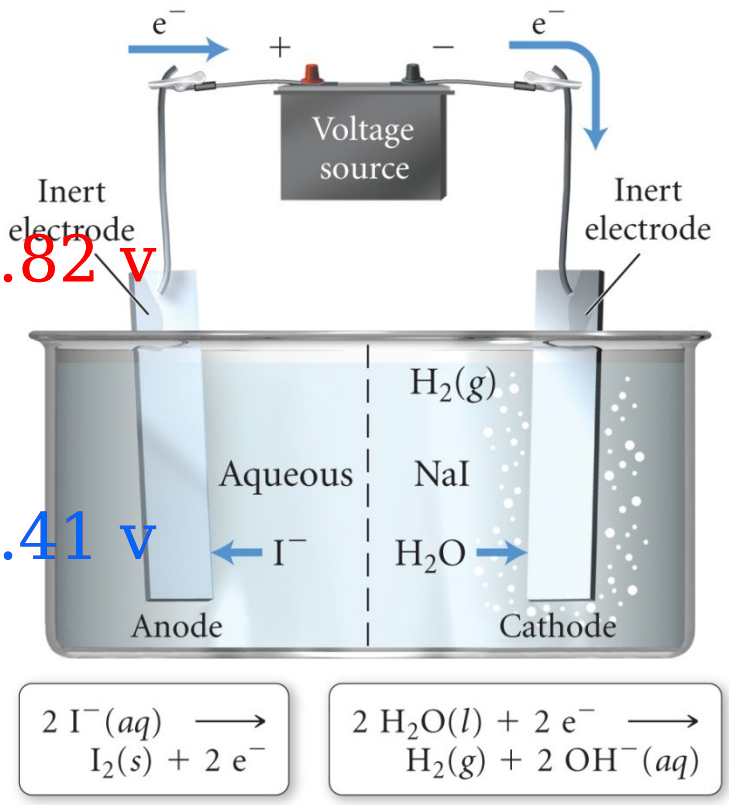
$I^{-1} \rightarrow I_2 + 2\ e^{-1}$ $\quad E° = -0.54$ v

$H_2O \rightarrow O_2 + 4e^{-1} + 4H^{+1}$ $\quad E° = -0.82$ v

ossible reductions

$a^{+1} + 1e^{-1} \rightarrow Na^0$ $\quad E° = -2.71$ v

$H_2O + 2\ e^{-1} \rightarrow H_2 + 2\ OH^{-1}$ $\quad E° = -0.41$ v

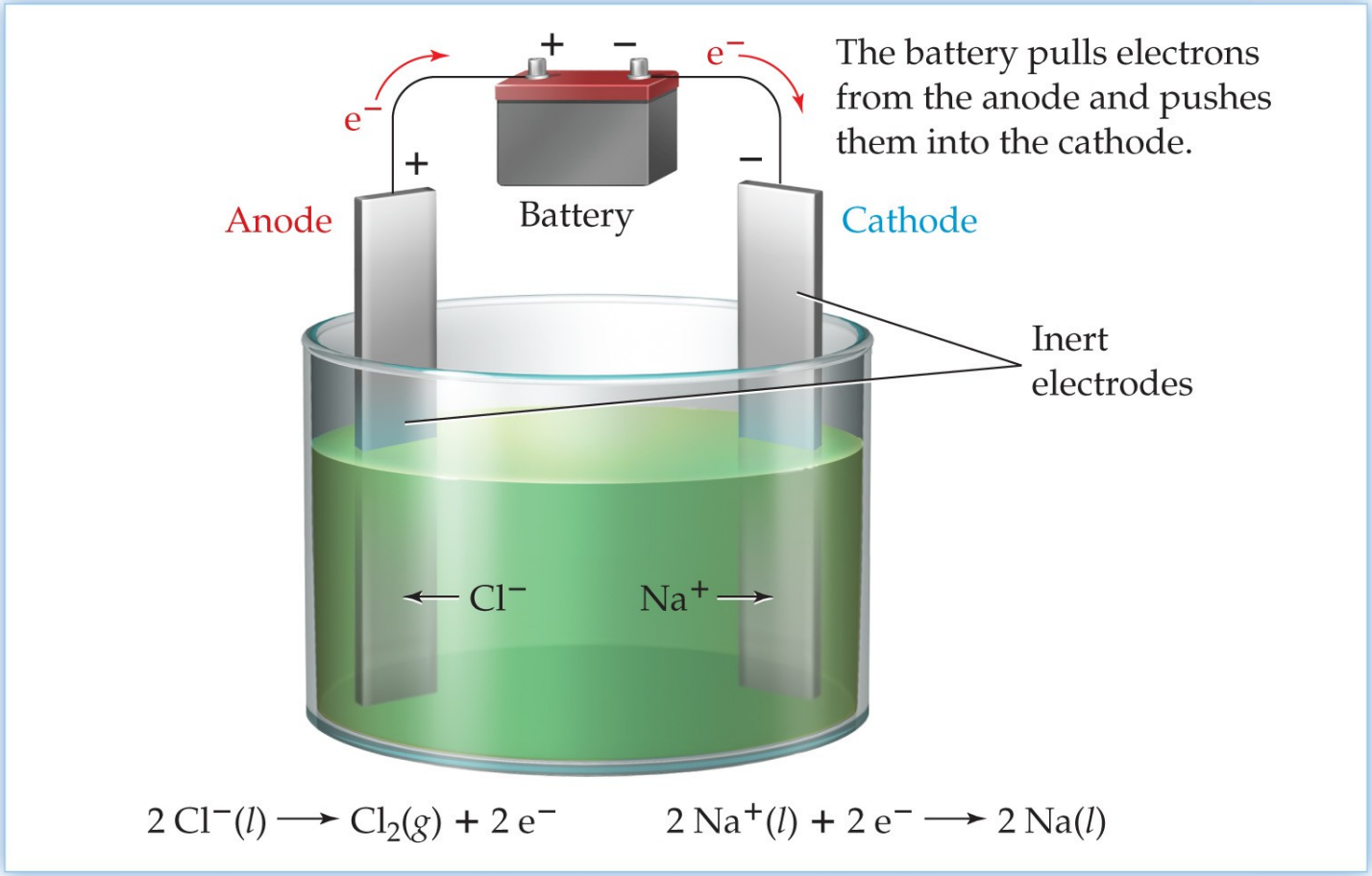


overall reaction

$2\ I^-_{(aq)} + 2\ H_2O_{(l)} \rightarrow I_{2(aq)} + H_{2(g)} + 2\ OH^{-1}_{(aq)}$

Electrolysis and Electrolytic Cells

Electrolysis of Molten Sodium Chloride



Electrolysis and Electrolytic Cells

Electrolysis of Aqueous Sodium Chloride

Anode: $2Cl^{1-}(aq) \longrightarrow Cl_2(g) + 2e^-$

Cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^{1-}(aq)$

Overall: $2Cl^{1-}(l) + 2H_2O(l) \longrightarrow Cl_2(g) + H_2(g) + 2OH^{1-}(aq)$

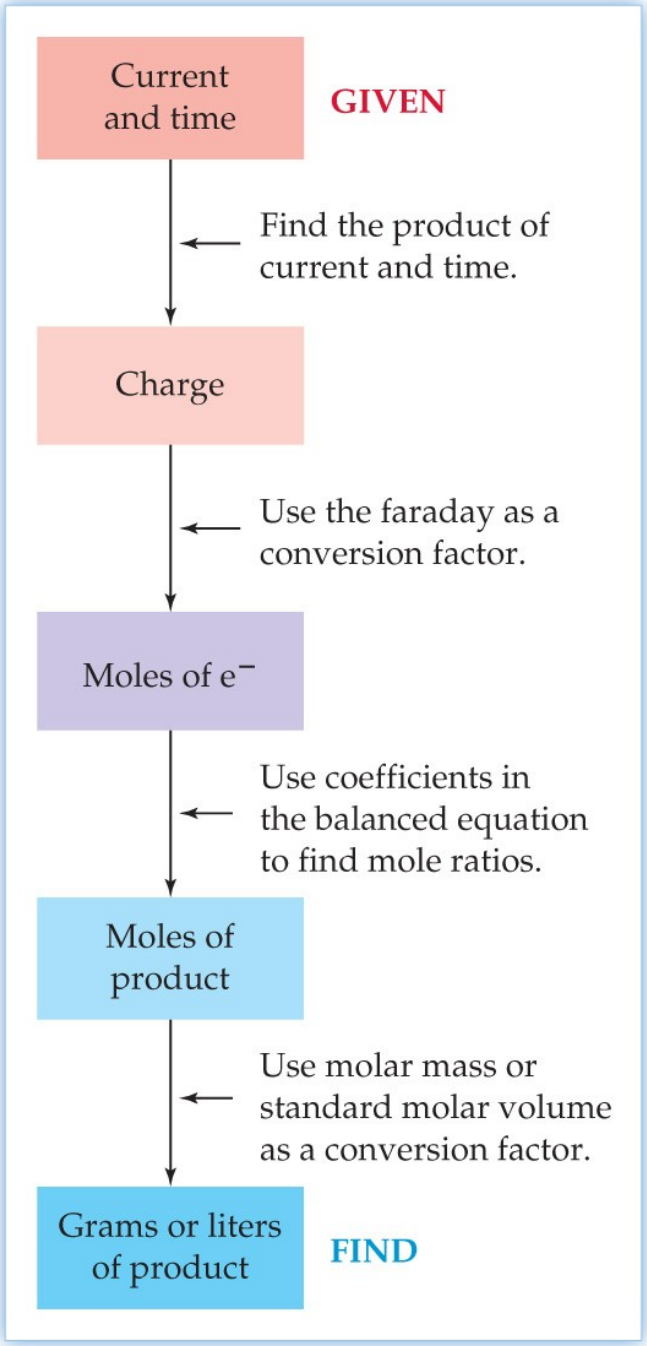
Electrolysis and Electrolytic Cells

Electrolysis of Water

Anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^{1+}(aq) + 4e^-$

Cathode: $4H_2O(l) + 4e^- \longrightarrow 2H_2(g) + 4OH^{1-}(aq)$

Overall: $6H_2O(l) \longrightarrow 2H_2(g) + O_2(g) + 4H^{1+} + 4OH^{1-}(aq)$


Current and time
GIVEN
Find the product of current and time.
Charge
Use the faraday as a conversion factor.
Moles of e⁻
Use coefficients in the balanced equation to find mole ratios.
Moles of product
Use molar mass or standard molar volume as a conversion factor.
Grams or liters of product
FIND

Quantitative Aspects of Electrolysis – Faraday's Law

$$\text{Charge(C)} = \text{Current(A)} \times \text{Time(s)}$$

$$\text{Moles of } e^- = \text{Charge(C)} \times \underbrace{\frac{1 \text{ mol } e^-}{96{,}500 \text{ C}}}_{\textbf{Faraday constant}}$$

Calculate the mass of Au that can be plated in 25 min using 5.5 A for the half-reaction

$$Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$$

Given:	3 mol e^- : 1 mol Au, current = 5.5 amps, time = 25 min
Find:	mass Au, g
Concept Plan:	t(s), amp → charge (C) → mol e^- → mol Au → g Au
Relationships:	$\frac{5.5\text{C}}{1\text{s}}$ $\quad \frac{1\text{mol}e^-}{96{,}485\text{C}}$ $\quad \frac{1\text{mol Au}}{3\text{mol}e^-}$ $\quad \frac{196.97\text{g}}{1\text{mol Au}}$
Solve:	$25\text{min} \times \frac{60\text{s}}{1\text{min}} \times \frac{5.5\text{C}}{1\text{s}} \times \frac{1\text{mol}e^-}{96{,}485\text{C}} \times \frac{1\text{mol Au}}{3\text{mol}e^-} \times \frac{196.97\text{g}}{1\text{mol Au}}$ $= 5.6\text{g Au}$
Check:	units are correct, answer is reasonable since 10 A running for 1 hr ~ 1/3 mol e^-

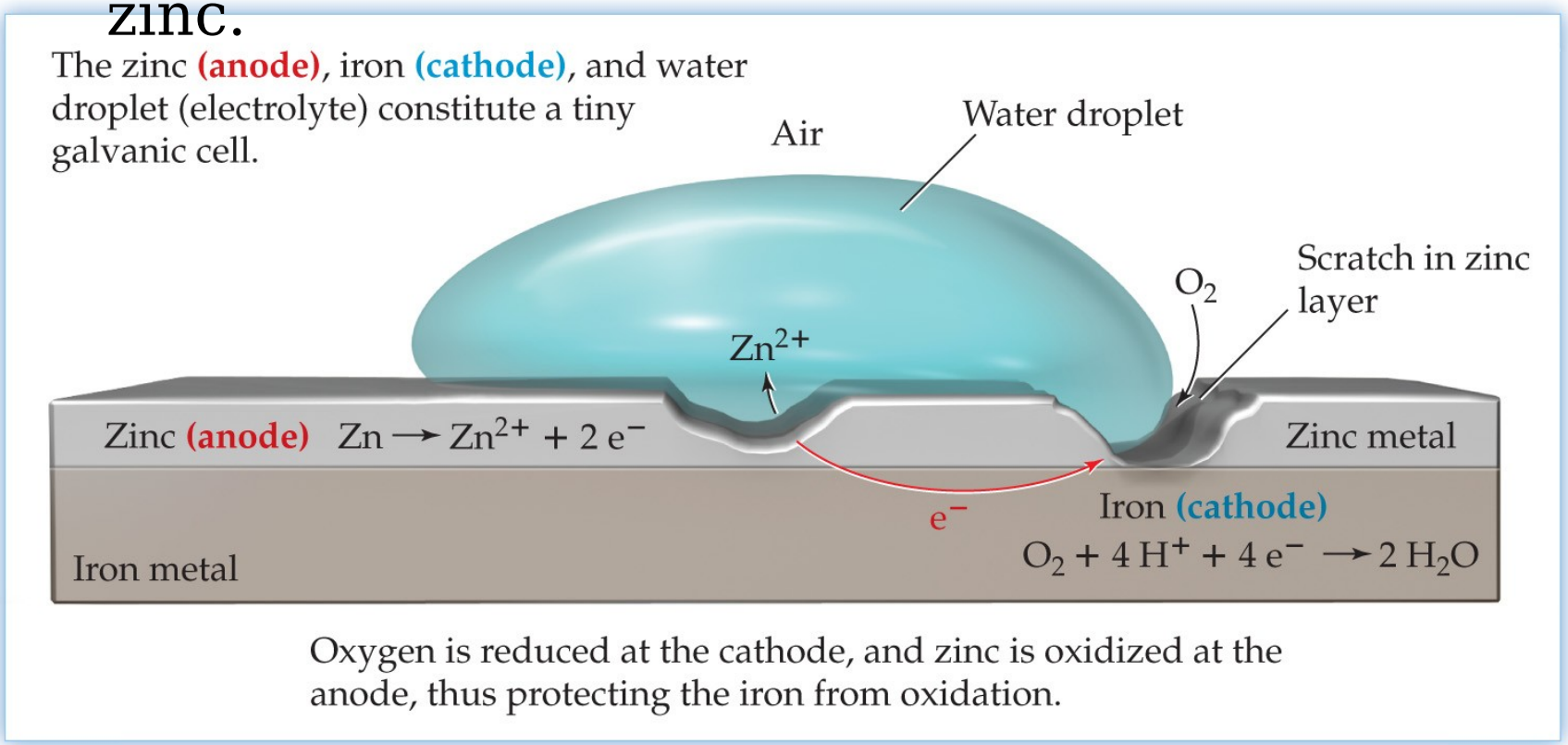
Corrosion

- **corrosion** is the spontaneous oxidation of a metal by chemicals in the environment
- since many materials we use are active metals, corrosion can be a very big problem

Corrosion Prevention

For some metals, oxidation protects the metal (aluminum, chromium, magnesium, titanium, zinc, and others). For other metals, there are two main techniques.

1. **Galvanization**: The coating of iron with zinc.



Oxygen is reduced at the cathode, and zinc is oxidized at the anode, thus protecting the iron from oxidation.

Corrosion Prevention

1. **Galvanization**: The coating of iron with zinc.

   When some of the iron is oxidized (rust), the process is reversed since zinc will reduce Fe^{2+} to Fe:

   $$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s) \quad E° = -0.45\ V$$

   $$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \quad E° = -0.76\ V$$

Corrosion Prevention

2. **Cathodic Protection**: Instead of coating the entire surface of the first metal with a second metal, the second metal is placed in electrical contact with the first metal:

Anode: $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$ $E° = 2.37$ V

Cathode: $O_2(g) + 4H^{1+}(aq) + 4e^- \longrightarrow 2H_2O(l)$ $E° = 1.23$ V

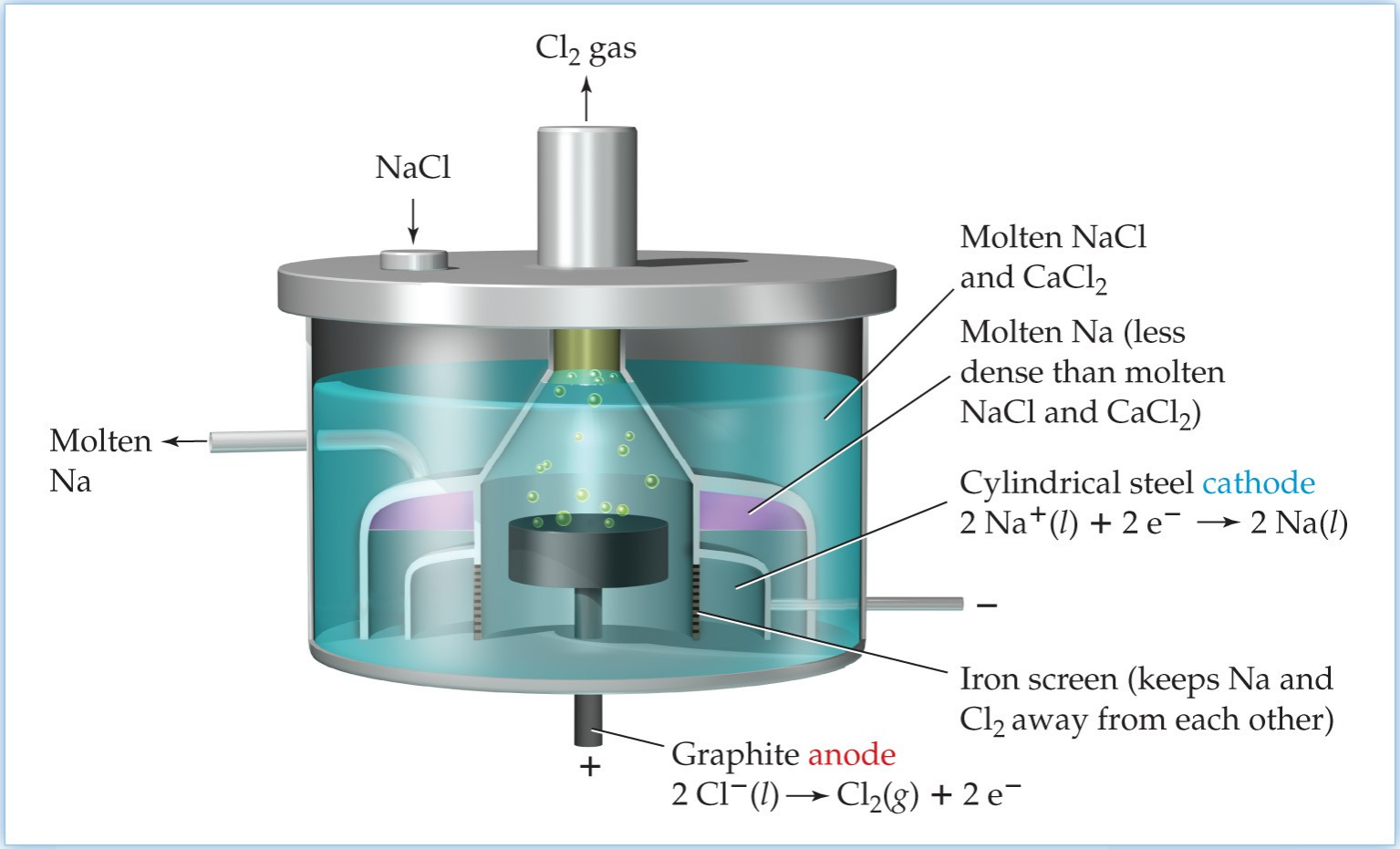
Attaching a magnesium stake to iron will corrode the magnesium instead of the iron. Magnesium acts as a *sacrificial anode*.

Rusting

- rust is hydrated iron(III) oxide
- moisture must be present
  - ✓water is a reactant
  - ✓required for flow between cathode and anode
- electrolytes promote rusting
  - ✓enhances current flow
- acids promote rusting
  - ✓lower pH = lower $E°_{red}$

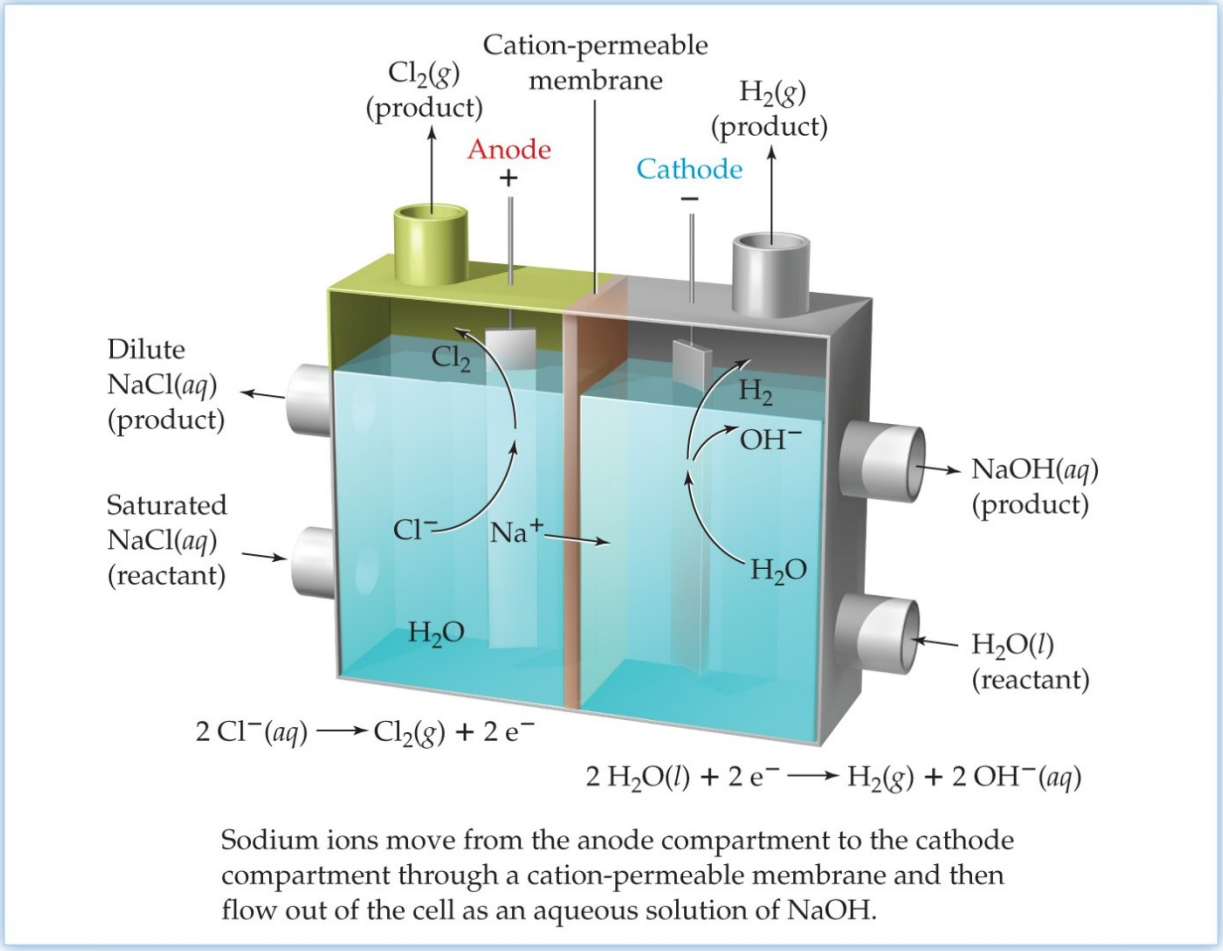
Commercial Applications of Electrolysis

Down's Cell for the Production of Sodium Metal


Cl_2 gas
NaCl
Molten NaCl and $CaCl_2$
Molten Na (less dense than molten NaCl and $CaCl_2$)
Molten Na
Cylindrical steel cathode
$2\ Na^+(l) + 2\ e^- \rightarrow 2\ Na(l)$
−
Iron screen (keeps Na and Cl_2 away from each other)
Graphite anode
$2\ Cl^-(l) \rightarrow Cl_2(g) + 2\ e^-$
+

Commercial Applications of Electrolysis

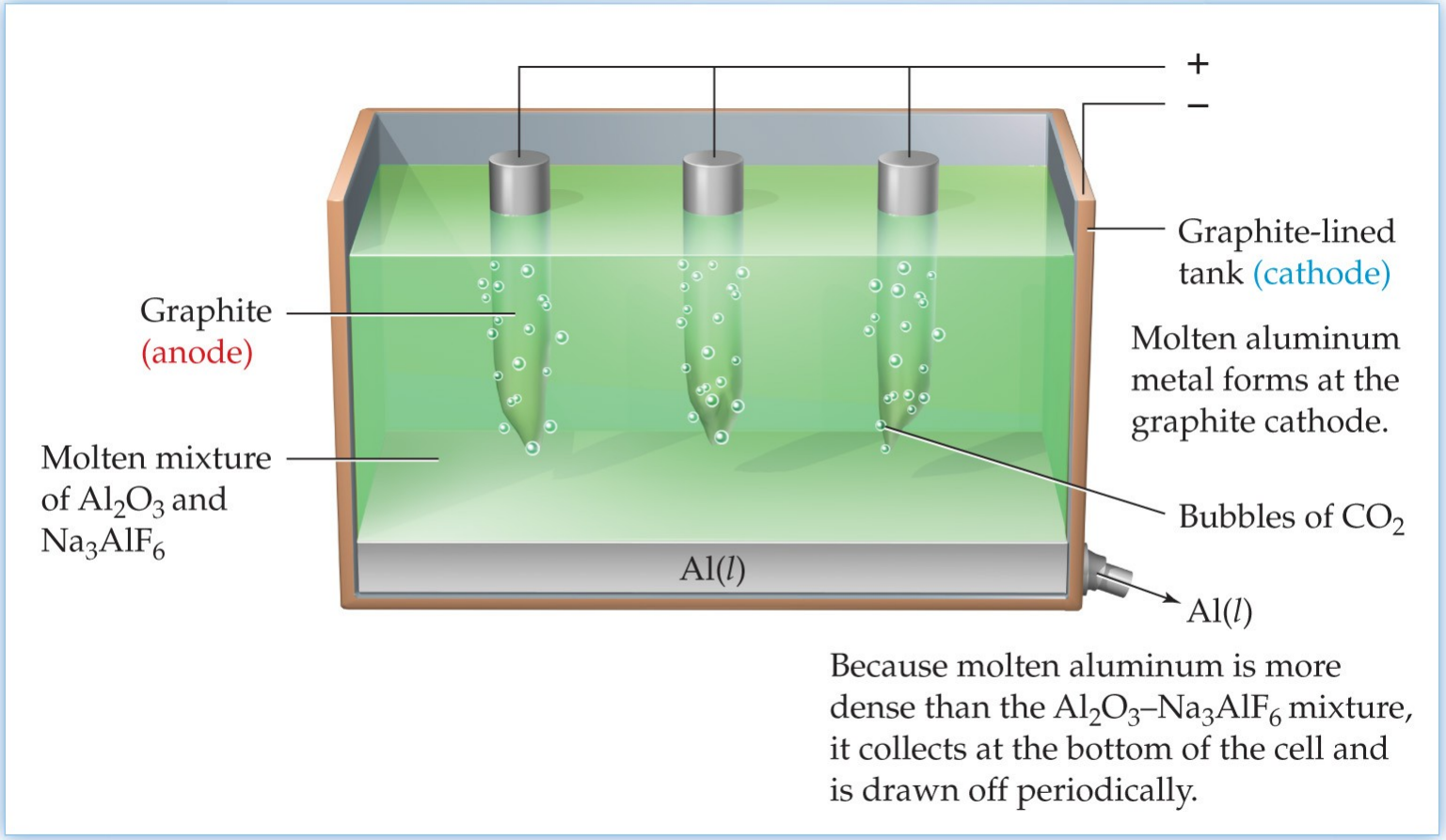
embrane Cell for Electrolytic Production of Cl_2 and Na



Sodium ions move from the anode compartment to the cathode compartment through a cation-permeable membrane and then flow out of the cell as an aqueous solution of NaOH.

Commercial Applications of Electrolysis

Hall-Heroult Process for the Production of Aluminum


+
−
Graphite-lined tank (cathode)
Graphite (anode)
Molten aluminum metal forms at the graphite cathode.
Molten mixture of Al_2O_3 and Na_3AlF_6
Bubbles of CO_2
Al(*l*)
Al(*l*)
Because molten aluminum is more dense than the Al_2O_3–Na_3AlF_6 mixture, it collects at the bottom of the cell and is drawn off periodically.

Commercial Applications of Electrolysis

Electrorefining of copper metal

Alternating slabs of impure copper and pure copper serve as the electrodes in electrolytic cells for the refining of copper.